PERKIN 1 COMMUNICATION

Ni(acac)$_2$-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodonium salts

Suk-Ku Kang,* Hyung-Chul Ryu and Sang-Woo Lee

Department of Chemistry, Sungkyunkwan University, Natural Science Campus,
Suwon 440-746, Korea

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The Ni-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodonium salts were achieved in the presence of Ni(acac)$_2$ (10 mol%) in NMP at 70 °C in moderate yields.

The palladium-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with organic electrophiles (*i.e.*, halides and triflates) are known as the Stille reaction[1] and have become an extremely powerful tool for carbon–carbon bond formation. In the search for alternatives to the palladium catalyst, the copper and manganese-catalyzed cross-coupling of organostannanes with organic halides has been reported.[2] Hypervalent iodine compounds have received much attention as the electrophiles with organostannanes in palladium-catalyzed reactions[3] due to their good reactivities, ready availability and nontoxic properties. Recently we have reported[4] copper(I)-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodine compounds. Here we wish to report nickel-catalyzed cross-coupling and carbonylative cross-coupling of iodonium salts with organostannanes.

Generally, to generate active nickel(0) species a reducing agent such as Zn, NaBH$_4$, or DIBAL-H is needed. Thus, in the nickel-catalyzed cross-coupling of organostannanes with arylmethanesulfonates by Percec *et al.*[5] the presence of zinc was essential to get an active catalyst. However in the literature, Ni(dppf)Cl$_2$-catalyzed cross-coupling of chloroarenes with arylboronic acids was realized in the absence of a reducing agent.[6] We have studied nickel-catalyzed cross-coupling and carbonylative cross-coupling of hypervalent iodonium salts with organostannanes and found that the catalyst Ni(acac)$_2$ is effective and surprisingly the catalyst performed much better when the reducing agent was omitted (Scheme 1).

$$R^1SnBu_3 \quad + \quad R^2I^+PhX^- \xrightarrow[\text{NMP, 70 °C, 8 h}]{\text{Ni(acac)}_2\text{ (10 mol\%)}} R^1\text{-}R^2$$

R^1 = Ph, *p*-MeOC$_6$H$_4$

X = BF$_4$, OTf, Br

R^2 = *p*-MeOC$_6$H$_4$, 2-thienyl, 2-furyl, (*E*)-PhCH=CH,

Scheme 1

Initially, we examined the cross-coupling of *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**1b**) with 2-thienyltributylstannane (**2c**) to form the coupled product **3g** and to find optimum conditions. After a series of experiments, it was found that of the catalysts tested [Ni(acac)$_2$, [Ni(acac)$_2$–Zn, NiCl$_2$(Ph$_3$P)$_2$, NiCl$_2$(Ph$_3$P)$_2$–Zn, NiCl$_2$(dppe), Ni(acac)$_2$–Zn–Ph$_3$P, Ni(acac)$_2$–Et$_2$Zn, Ni(acac)$_2$–ZnCl$_2$, NiCl$_2$(dppe)–Zn, NiCl$_2$] Ni(acac)$_2$ was the only catalyst which afforded the coupled product in a high yield. Of the solvents tested (NMP, DMF, CH$_3$CN, CHCl$_3$, THF, CHCl$_3$–NMP) the solvents NMP and DMF were effective and NMP was the best choice.

The nickel-catalyzed cross-coupling of hypervalent iodonium salts with organostannanes is summarized in Table 1. The diphenyliodonium tetrafluoroborate (**1a**) reacted with 2-thienyltributylstannane (**2c**) in the presence of Ni(acac)$_2$ (10 mol%) in NMP at 70 °C for 8 h to afford 2-phenylthiophene (**3a**)[7] in 79% yield (entry 1 in Table 1). Under the same conditions, treatment of the iodonium salt **1a** with 2-furyltributylstannane (**2d**) gave 2-phenylfuran (**3b**)[8] in 78% yield (entry 2). This coupling was applied to alkenyl- and alkynylstannane **2e** and **2f**. The iodonium salt **1a** was readily coupled with **2e** and **2f** to provide the coupled alkene **3c** and alkyne **3d** in 82 and 80% yields, respectively (entries 3 and 4) (see Experimental section). For the *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**1b**), reaction with *p*-methoxyphenyltributylstannane (**2b**) gave 4,4′-dimethoxy-1,1′-biphenyl (**3e**) in 73% yield (entry 5). Coupling of **1b** with 2-furyl- and 2-thienyltributylstannane (**2d**) and (**2c**) afforded *p*-methoxyphenyl-substituted furan and thiophene **3f** and **3g**[9] in 71 and 77% yields, respectively (entries 6 and 7). For the *p*-methoxyphenyl(phenyl)iodonium triflate and bromide (**1c**) and (**1d**), which have different counterions from **1b**, reaction with **2c** afforded the coupled product **3g** in 75 and 78% yields (entries 8 and 9). It is notable that the yields of cross-coupling were not dependent on the counterions.

In considering a plausible mechanism for the coupling, it is presumed that the oxidative addition of highly reactive electrophilic iodonium salt **1a** with Ni(0) gives polar and reactive PhNi(II)L$_2$, which if subjected to transmetallation with organostannanes followed by reductive elimination would give the cross-coupled product.

This cross-coupling was extended to carbonylation cross-coupling and the results of carbonylative cross-coupling of hypervalent iodonium salts with organostannanes under atmospheric pressure are summarized in Scheme 2 and Table 2.

$$R^1SnBu_3 \quad + \quad R^2I^+PhBF_4 \xrightarrow[\substack{\text{NMP, 70 °C, 8 h} \\ \text{CO (1 atm)}}]{\text{Ni(acac)}_2\text{ (10 mol\%)}} R^1COR^2$$

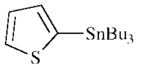
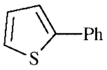
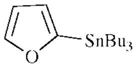
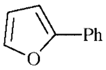
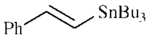
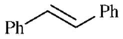
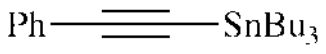
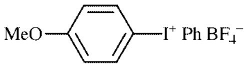
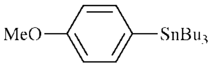
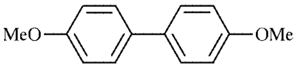
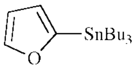
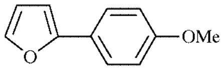
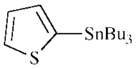
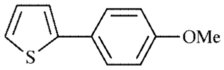
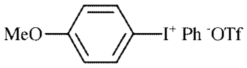
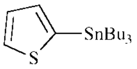
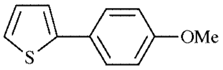
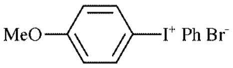
R^1 = Ph, *p*-MeOC$_6$H$_4$, (*E*)-PhCH=CH

R^2 = Ph, 2-thienyl, 2-furyl, (*E*)-PhCH=CH,

Scheme 2

The iodonium salt **1a** reacted with phenyltributylstannane (**2a**) in the presence of Ni(acac)$_2$ (10 mol%) in NMP under an atmospheric pressure of carbon monoxide at 70 °C for 8 h to afford benzophenone (**4a**) in 81% yield (entry 1 in Table 2) (see Experimental section). Under the same conditions, 2-thienyltributylstannane (**2c**) was readily coupled with carbon monoxide to give the ketone **4b**[10] in 76% yield (entry 2). This carbonylative cross-coupling was applied to alkenyl- and alkynyl-substituted stannanes **2e** and **2f** which were smoothly coupled to afford unsaturated ketones **4c** and **4d**[11] in 72 and 78% yields, respectively (entries 3 and 4). For *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**1b**), 2-thienyltributylstannane (**2c**) was readily coupled under CO to give aryl

Table 1 Ni(acac)$_2$-catalyzed cross-coupling of organostannanes with hypervalent iodonium salts

Entry	Hypervalent iodonium salts	Organostannanes	Product	Isolated yield (%)
1	Ph$_2$I$^+$BF$_4^-$ **1a**	 **2c**	 **3a**	79
2	**1a**	 **2d**	 **3b**	78
3	**1a**	 **2e**	 **3c**	82
4	**1a**	 **2f**	 **3d**	80
5	 **1b**	 **2b**	 **3e**	73
6	**1b**	 **2d**	 **3f**	71
7	**1b**	 **2c**	 **3g**	77
8	 **1c**	 **2c**	 **3g**	75
9	 **1d**	**2c**	**3g**	78

ketone **4e**[10] in 70% yield (entry 5). Treatment of **1b** with alkynyl-substituted stannane **2f** afforded ynone **4f**[12] in 69% yield (entry 6). Finally the alkenyl-substituted iodonium salt **1c** was reacted with 2-furyltributylstannane (**2d**) to afford the enone **4g**[13] in 65% yield (entry 7).

Experimental

Typical procedure

To a mixture of diphenyliodonium tetrafluoroborate (**1a**) (500 mg, 1.36 mmol) and nickel(II) acetylacetonate (34.9 mg, 10 mol%) was added tributyl(phenylethynyl)stannane (**2f**) (532 mg, 1.36 mmol) under N_2 charged at 70 °C in NMP (20 ml). The reaction mixture was stirred at 70 °C for 8 h, extracted with ether (20 mL × 3) and washed with water (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, $R_f = 0.49$) to afford diphenylacetylene (**3d**) (194 mg, 80%).

To a mixture of diphenyliodonium tetrafluoroborate (**1a**) (500 mg, 1.36 mmol) and nickel(II) acetylacetonate (34.9 mg, 10 mol%) was added tributylphenylstannane (**2a**) (499 mg 1.36 mmol) under atmospheric CO at 70 °C in NMP (20 ml). The reaction mixture was stirred at 70 °C for 8 h, extracted with ether (20 mL × 3), and washed with water (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc–hexanes 1:10 $R_f = 0.45$) to afford benzophenone (**4a**) (200 mg, 81%).

Acknowledgements

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Notes and references

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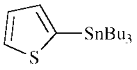
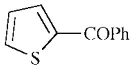
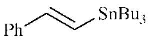
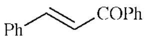
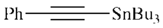
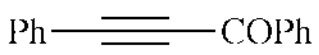
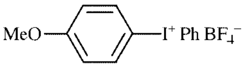
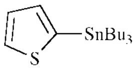
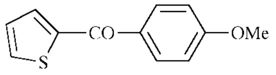
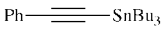
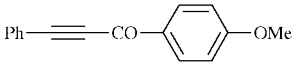
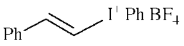
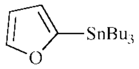
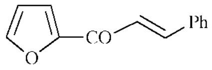
Table 2 Ni(acac)$_2$-catalyzed carbonylative cross-coupling of organostannanes with hypervalent iodonium salts

Entry	Hypervalent iodonium salts	Organostannanes	Product	Isolated yield (%)
1	$Ph_2I^+BF_4^-$ **1a**	$PhSnBu_3$ **2a**	PhCOPh **4a**	81
2	**1a**	 **2c**	 **4b**	76
3	**1a**	 **2e**	 **4c**	72
4	**1a**	 **2f**	 **4d**	78
5	 **1b**	 **2c**	 **4e**	70
6	**1b**	 **2f**	 **4f**	69
7	 **1c**	 **2d**	 **4g**	65

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