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Manganese Chloride-Catalyzed Cross-Coupling and Carbonylative Cross-Coupling of Organostannanes with Iodonium Salts

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Abstract: *The $MnCl_2$•$4H_2O$-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodonium salts afforded biaryls and biaryl ketones, respectively.*

The palladium-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with aryl halides, known as the Stille reaction has developed into an extremely powerful tool for the construction of carbon-carbon bonds.[1,2] As alternatives to organic electrophiles, recently we have reported the palladium-catalyzed[3] and copper-catalyzed[4] cross-coupling and carbonylative cross-coupling of hypervalent iodonium salts with organostannanes. Alternatively, we have investigated copper iodide and manganese bromide-catalyzed cross-coupling of organostannanes with organic iodide in the presence of NaCl.[5] Here, we wish to report manganese chloride-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with iodonium salts. The organostannane **1a** was reacted with diphenyliodonium tetrafluoroborate (**2a**) in NMP/THF (1 : 1) at 70 °C using $MnCl_2$•$4H_2O$ (5 mol %) as a catalyst to afford biphenyl **3a** in 72% yield. Of the manganese catalysts tested $MnCl_2$•$4H_2O$ was the best choice and $MnBr_2$ was not effective. Accordingly, when 2-thienyl- and 2-furyl-substituted organostannanes **1b** and **1c** were treated with iodonium salt **2a** under the same conditions to give **3b** and **3c** in 80 and 84% yields, respectively.[6] The yields of the coupled products were highly dependent on the solvents employed and the cosolvent system THF/NMP (1 : 1) were the best choice. In the coupling reaction of organostannane **1b** with iodonium salt **2a** the influence of cosolvent NMP was remarkable. The yield in THF and NMP were 30% or 62%, respectively. However, with THF/NMP (1 : 1) the yield was improved to 80%. This method was applied to alkenyl-substituted iodonium salt **2b** and 2-thienyl-substituted organostannane **1b** was coupled to give the alkenyl-substituted thiophene **3d** (48%) along with the homocoupled bithiophene (20%). For the (*p*-methoxyphenyl)phenyliodonium tetrafluoroborate (**2c**) coupling with **1b** and **1c** provided **3f** and **3g** in 54 and 61% yields. By similar method, alkenyl-substituted organostannane **1d** was successfully coupled with **2a** to afford (*E*)-stilbene (**3h**) in 67% yield. When this coupling was applied to alkynyl-substituted organostannane **1e** and **2a**, the coupled product **3k** was afforded (Scheme 1).

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$$R^1SnBu_3 + R^2I^+Ph\,BF_4^- \xrightarrow[\text{NMP/THF, 70 °C}]{MnCl_2•4H_2O\text{ (5 mol \%)}} R^1\text{-}R^2$$

$\mathbf{1}$ $\mathbf{2}$ $\mathbf{3}$

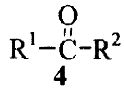
1a R^1 = Ph
1b R^1 = 2-thienyl
1c R^1 = 2-furyl
1d R^1 = (*E*)-PhCH=CH
1e R^1 = PhC≡C
2a R^2 = Ph
2b R^2 = (*E*)-PhCH=CH
2c R^2 = *p*-MeOC_6H_4

3a R^1 =Ph, R^2 = Ph (72%)
3b R^1 = 2-thienyl, R^2 = Ph (80%)
3c R^1 = 2-furyl, R^2 = Ph (84%)
3d R^1 = 2-thienyl, R^2 = (*E*)-PhCH=CH(48%)
3e R^1 = 2-furyl, R^2 = (*E*)-PhCH=CH(47%)
3f R^1 = 2-thienyl, R^2 = *p*-MeOC_6H_4 (54%)
3g R^1 = 2-furyl, R^2 = *p*-MeOC_6H_4 (61%)
3h R^1 = (*E*)-PhCH=CH, R^2 = Ph (67%)
3i R^1 = PhC≡C, R^2 = Ph (72%)

Scheme 1

We extended this coupling to organostannane **1b** in carbonylative coupling with **2a** under atmospheric pressure of CO at 60 °C in THF/NMP, 2-benzylfuran (**4a**) was readily obtained in 82% yield. Similarly, the carbonylative-coupling of **1c** with **2a** proceeded smoothly with CO (1 atm) to give 2-benzoylfuran (**4b**) in 81% yield. For the alkenyl-substituted iodonium salt **2b**, treatment of organostsnnane **1b** with CO(1 atm) gave the α,β-unsaturated ketone **4c** in 43% yield together with 2-benzoylthiophene (25%). The organostannane **1c** was carbonylated to give ketone **4d**(51%) and 2-benzoylfuran (28%)(Scheme 2).

$$R^1SnBu_3 + R^2I^+Ph\,BF_4^- \xrightarrow[\text{CO (1 atm), 60 °C, NMP/THF}]{MnCl_2•4H_2O\text{ (5 mol \%)}}$$



$R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2$

$\mathbf{1}$ $\mathbf{2}$ $\mathbf{4}$

1b R^1 = 2-thienyl
1c R^1 = 2-furyl
2a R^2 = Ph
2b R^2 = (*E*)-PhCH=CH

4a R^1 = 2-thienyl, R^2 = Ph (82%)
4b R^1 = 2-furyl, R^2 = Ph (81%)
4c R^1 = 2-thienyl, R^2 = (*E*)-PhCH=CH(43%)
4d R^1 = 2-furyl, R^2 = (*E*)-PhCH=CH(51%)

Scheme 2

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6. The typical procedure is as follows. To a stirred solution of $Ph_2I^+BF_4^-$ (100 mg, 0.27 mmol) and $MnCl_2•4H_2O$ (2.7 mg, 5 mol %) in THF/NMP (2 : 1, 3 mL) at 70 °C was added the organostannane **1b** (110 mg, 0.30 mmol) in NMP (1 mL). The reaction mixture was heated at reflux for 15 h and cooled to room temperature. The mixture was extracted with ether and 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 = 0.43) to afford 2-phenylthiophene (**3b**) (34.8 mg, 80%).