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

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Abstract: The MnCl₂•4H₂O-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodonium salts afforded biaryls and biaryl ketones, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

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 palladiumcatalyzed³ and copper-catalyzed⁴ cross-coupling and carbonylative cross-coupling of hypervalent iodonium salts with organostannanes. Alternatively, we have investigated copper iodide and manganese bromidecatalyzed 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 MnCl₂•4H₂O (5 mol %) as a catalyst to afford biphenyl 3a in 72% yield. Of the manganese catalysts tested MnCl₂•4H₂O was the best choice and MnBr₂ 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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$$\begin{array}{c} R^{1}SnBu_{3} + R^{2}I^{+}Ph \ BF_{4}^{-} \\ 1 \\ 2 \\ 1 \\ R^{1} = Ph \\ 1b \ R^{1} = 2\text{-thienyl} \\ 1c \ R^{1} = 2\text{-furyl} \\ 1d \ R^{1} = (E)\text{-PhCH=CH} \\ 1e \ R^{1} = Ph \ C^{=}C \\ 2a \ R^{2} = Ph \\ 2b \ R^{2} = (E)\text{-PhCH=CH} \\ 2c \ R^{2} = p\text{-MeOC}_{6}H_{4} \\ \end{array}$$

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).

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References and Notes

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- 6. The typical procedure is as follows. To a stirred solution of Ph₂I BF₄ (100 mg, 0.27 mmol) and MnCl₂•4H₂O (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 MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (hexanes, $R_f = 0.43$) to afford 2-phenylthiophene (**3b**) (34.8 mg, 80%).