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Copper-Catalyzed Coupling of Polymer Bound Iodide with Organostannanes

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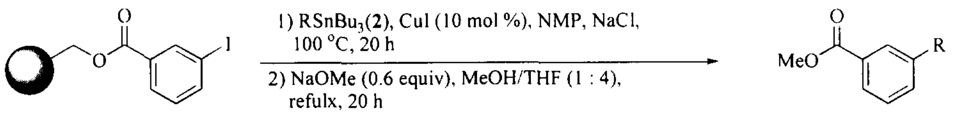
Abstract: *The copper iodide-catalyzed cross-coupling of polymer bound aryl iodide with organostannanes in N-methyl-2-pyrrolidone (NMP) was accomplished smoothly in the presence of NaCl.* © 1998 Elsevier Science Ltd. All rights reserved.

Recently, advantages of solid phase organic chemistry for constructing libraries of organic molecules are well recognized in combinatorial synthesis.[1] Palladium-catalyzed coupling reactions have been developed as suitable techniques for solid phase synthesis[2] including cross-coupling of organostannanes with polymer bound aryl iodide.[3] Here we wish to report the cuprous iodide-catalyzed cross-coupling[4] of organostannanes with polymer-bound aryl iodide in the presence of sodium chloride (Eq. 1).



1

3

R = phenyl-, 2-furyl, vinyl,
β-styryl, phenylacetylenic

Commercially available Merrifield resin reacted with 3-iodobenzoic acid to give polymer bound 3-iodobenzoic acid(**1**).[5] This polymer bound 3-iodobenzoic acid was subjected to CuI (10 mol %)-catalyzed cross-coupling reactions with a variety of stannanes **2** followed by transesterification to afford the substituted esters **3**,[6] the results of which are shown in Table 1. Typical procedure for the cross-coupling reaction is as follows. To a degassed suspension of polymer bound aryl iodide **1** in anhydrous NMP (3 mL) was added CuI (10 mol %) followed by NaCl (2 equiv). The mixture was stirred at 100 °C for 5 min and organostannane **2a** in NMP (7 mL) was then slowly added *via* syringe pump over 4 h at 100 °C. The reaction mixture was allowed to stir at 100 °C for 20 h, transferred to a glass filter, and thoroughly washed with CH_2Cl_2, MeOH, DMF, MeOH, and then CH_2Cl_2. Cleavage of the product from resin was achieved readily by transesterification (0.6 equiv NaOMe, MeOH/THF (1 : 4), reflux for 20 h) to provide the biaryl ester **3a**[6] in 89% yield.[7]

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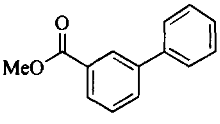
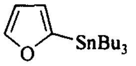
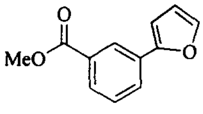
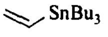
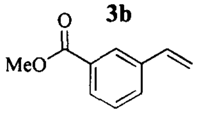
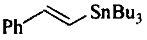
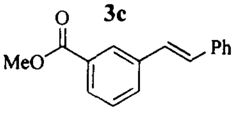
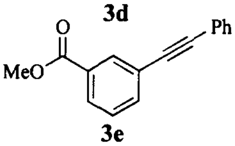
Table 1. Cuprous Iodide-Catalyzed Coupling of Polymer Bound Iodide(**1**) with Organostannanes(**2**)

Entry	Stannanes	Products[6]	Yield(%)
1	$\mathrm{PhSnBu_3}$ **2a**	 **3a**	89
2	 **2b**	 **3b**	94
3	 **2c**	 **3c**	55
4	 **2d**	 **3d**	83
5	$\mathrm{Ph{-}{\equiv}{-}SnBu_3}$ **2e**	 **3e**	78

Acknowledgment. We gratefully acknowledge the financial support from Korea Reserch Foundation, Non-directed Fund (No. 1997-001-D00241).

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6. Satisfactory spectral data were obtained in accordance with the structure. Selected spectral data are as follows. **3a**: ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 3.96 (s, 3H), 7.43(m, 1H),7.50 (m, 3H), 7.63 (m, 2H), 7.85 (m, 1H), 8.03(m, 1H), 8.29 (m, 1H). MS (EI): m/e = 212 ($\mathrm{M^+}$, 83), 181 (100), 152 (63), 76 (32). **3d**: ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 3.95 (s, 3H), 7.15 (m, 1H), 7.20 (d, 1H, J = 16 Hz), 7.28 (d, 1H, J = 16 Hz), 7.36(m, 1H), 7.42 (m, 3H), 7.54 (m, 2H), 7.69 (m, 1H), 8.20 (m, 1H). MS (EI): m/e = 238 ($\mathrm{M^+}$, 42), 205 (22), 178 (100), 89 (14), 77 (4). **3e**: ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 3.94 (s, 3H), 7.36 (m, 3H), 7.44 (m, 1H), 7.55 (m, 2H), 7.70 (m, 1H), 7.99 (m, 1H), 8.21 (m, 1H). MS (EI): m/e = 236 ($\mathrm{M^+}$, 100), 176 (64), 151 (21), 102 (19), 88 (32).
7. The yield was calculated based on the amount of polymer bound aryl iodide which was transesterified.