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Copper- and Manganese-Catalyzed Homocoupling of Organostannanes in the Presence of Iodine

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Abstract

The copper- and manganese-catalyzed homocoupling of aryl-, alkenyl-, and alkynylstannanes to afford biaryls, 1,3-dienes, and 1,3-diynes were achieved in the presence of iodine at 100 °C in good yields.

Keywords: biaryls; coupling reactions; tin and compounds; copper and compounds; manganese and compounds

The oxidative homocouping of aryl, alkenyl-, and alkynyl-substituted stannanes is one of the useful synthetic methods to form symmetrical biaryls, 1,3-dienes, and 1,3-diynes. Thus, the palladium-catalyzed homocoupling of organostannanes was reported employing *t*-BOOH [1], benzoquinone [2], HMPA [3], dichloroethane [4], diiodoethene [5], chloroacetone [6], acrylate dibromide [7], and air [8,9] as oxidant. Efficient homocoupling of stoichometric amounts of copper salts have been already reported [10]. However, copper-catalyzed reactions have not been realized, in spite of their great potentials. Here we report that copper(II) chloride and manganese bromide efficiently catalyze the homocoupling of aryl-, alkenyl-, and alkynylstannanes by the use of iodine as an oxidant.

$$\underset{\mathbf{1}}{2\ \mathrm{RSnBu_3}} \xrightarrow[\mathrm{I_2\ (0.5\ equiv),\ DMF\ or\ NMP,\ 100\ ^\circ C}]{\mathrm{CuCl_2\ or\ MnBr_2\ (10\ mol\ \%)}} \underset{\mathbf{2}}{\mathrm{R\text{-}R}}$$

1a R = Ph, **1b** R = 2-pyridyl
1c R = 2-furyl, **1d** R = 2-thienyl
1e R = p-MeOC$_6$H$_4$, **1f** R = (E)-PhCH=CH
1g R = PhC≡C

2a R = Ph, **2b** R = 2-pyridyl
2c R = 2-furyl, **2d** R = 2-thienyl
2e R = p-MeOC$_6$H$_4$, **2f** R = (E)-PhCH=CH
2g R = PhC≡C

Scheme 1

To find suitable reaction conditions, we have examined the homocoupling of 1-phenylalkynylstannanes **1g**. Using CuI or CuCl (10 mol %) as catalyst in DMF at 60 °C or 100 °C the yield became lower (20~30 %) even in the presence of CsF or KF as additive. We found that by slow addition of I_2 (0.5 equiv) for 4 h the yield improved to more than >95% after isolation. As suitable catalysts, CuI, CuCl, $CuCl_2$, and $CuF_2 \cdot 2H_2O$ tested, $CuCl_2$ was the best of

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choice. At 65 °C for 4 h we could get the product a rather lower (45%) yield.

However at 100 °C almost quantitative yield of the dimerized product was obtained. In the case of $MnBr_2$ (10 mol %) as catalyst, of the solvent THF, dioxane, DMF, and NMP, NMP was the most suitable. In considering the role of I_2 in these catalytic reactions, it is presumed that iodine might act as an oxidant or a scavenger for organostannanes. The results are summarized in Table 1 [11].

In conclusion, the catalytic oxidative homocoupling of organostannanes was accomplished by $CuCl_2$ or $MnBr_2$ adding slowly iodine as an oxidant.

Table 1.Copper- and Manganese-Catalyzed Homocoupling of Organostannanes in the Presence of Iodine

Entry	Substrate	Reaction Conditions [a]	Time	Product	Yield (%) [b]
1	**1a**	A	4	**2a**	93
		B	5		70
2	**1b**	A	4	**2b**	85
3	**1c**	A	4	**2c**	80
		B	5		80
4	**1d**	A	4	**2d**	72
		B	5		83
5	**1e**	A	4	**2e**	74
		B	5		85
6	**1f**	A	4	**2f**	68
		B	5		90
7	**1g**	A	4	**2g**	95
		B	5		81

[a] A: $CuCl_2$(10 mol %), I_2(0.5 equiv), DMF, 100 °C. B: $MnBr_2$ (10 mol %), I_2(0.5 equiv), NMP, 100 °C.

[b] The isolated yields.

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[11] The typical procedure is as follows. **Method A**: To a stirred solution of $CuCl_2$ (17.2 mg, 10 mol %) and DMF (5 mL) was added **1g** (500 mg, 1.28 mmol). The reaction mixture was heated to reflux at 100 °C and then I_2 (162 mg, 0.50 equiv) in DMF (5 mL) was added *via* syringe pump for 4 h. When the addition was completed checked by tlc or gc, the reaction mixture was cooled to room temperature and quenched with saturated KF solution. The reaction 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 = 0.38) to afford 1,4-diphenylbutadiyne (**2g**) (123 mg, 95%). **Method B**: To a stirred solution of $MnBr_2$ (29 mg, 10 mol %) and NMP (5 mL) was added **1a** (500 mg, 1.36 mmol). The reaction mixture was heated to reflux at 100 °C and then I_2 (173 mg, 0.50 equiv) in NMP (5 mL) was added *via* syringe pump for 5 h. When the addition was completed checked by tlc or gc, the reaction mixture was cooled to room temperature and quenched with saturated KF solution. The reaction 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 = 0.50) to afford biphenyl (**2a**) (74 mg, 70%).