Preparation of Aryltributyltin Having Electron-withdrawing Group by Palladium Catalyzed Reaction of Hexabutylditin with Aryl Iodide

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Synopsis. Nitro-, acyl-, and cyanophenyltributyltin can be prepared by the reaction of hexabutylditin with the corresponding aryl iodide in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium.

Aryltin compounds are generally prepared by the reaction of an aryl organometallic (Grignard or lithium) reagent with organotin halide or by the reaction of organotin lithium with aryl halide.[1] However, aryltin compound in which the aryl groups bear reactive functional substituents (*e.g.* $-NO_2$, $-COR$, $-CN$ *etc.*) cannot be prepared by these methods, because the functional groups are sensitive to the lithium or magnesium reagent. In our previous communication we reported that the palladium-catalyzed reaction of hexabutylditin with aryl bromides is a promising tool to prepare such aryltributyltins, although biaryls are produced as by-products.[2] About the same time, similar trials were also reported by two groups.[3,4] However, optimum reaction conditions for the preparation of nitrophenyltributyltin seem not to be attained.[3] This note describes our results for preparation of these compounds by the method, showing that aryl iodides are better substrates than the bromides.

$$Bu_3SnSnBu_3 + ArX \xrightarrow{Pd(PPh_3)_4} ArSnBu_3 + Bu_3SnX$$

The reaction were carried out by heating a stirred solution of an aryl iodide, 1.5 molar excess of hexabutylditin and a catalytic amount of tetrakis(triphenylphosphine)palladium in toluene at 60 °C for 72 h under argon. After evaporation to remove the solvent, the residue was washed with aqueous potassiun fluoride to remove tributyltin iodide by converting into insoluble tributyltin fluoride. The organic layer was extracted with benzene and dried over sodium sulfate. Purification was performed by column chromatography. The results are presented in Table 1.

Nitro-, cyano-, and acetylphenyltributyltins are obtained in good yields. It is important to note that the usage of mild reaction conditions is necessary to avoid the formation of biaryl, because aryltributyltin formed can react with aryl halide in the presence of the same catalyst, particularly easily at higher temperature.

$$ArSnBu_3 + ArX \xrightarrow{Pd(PPh_3)_4} ArAr + Bu_3SnX$$

The reaction with aryl iodide at 60 °C gave good results enough for the synthetic purpose. In the reaction of *o*-nitrophenyl iodide, no biaryl was obtained, probably due to the steric effect, and yield of aryltin compound was almost quantitative even at higher temperature.

Table 1. Palladium-catalyzed reaction of hexabutylditin with aryl iodide

Y-C_6H_4-I(-Br) Y	Temp/°C	Yield of Y-C_6H_4-$SnBu_3$/%[a] Y		
p-NO_2	80	*p*-NO_2	30[b]	(38)
	60		63	
m-NO_2	60	*m*-NO_2	65	(23)
o-NO_2	80	*o*-NO_2	98	(59)
p-Ac	60	*p*-Ac	83	(21)
p-CN	60	*p*-CN	85	(22)

a) Isolated yield based on the iodide. In parenthesis, yield from aryl bromide at 80 °C. b) GLC yield.

Experimental

IR spectra were recorded on a Hitachi EPI-3G spectrophotometer. NMR spectra were recorded on a Varian EM-360 instrument. GLC analyses were carried out with an Ohkura 802 instrument, using column (1.5 m) packed with 10% Silicone SF-96, 10% SE-30, and 10% Carbowax-20M on Celite 545 (AW DMCS).

Materials. Hexabutylditin,[5] $Pd(PPh_3)_4$,[6] *o*-, *m*-, and *p*-iodonitrobenzene,[7] *p*-iodoacetophenone,[8] and *p*-iodobenzonitrile[9] were prepared by the methods described in literatures.

Reaction Procedure. A stirred solution of hexabutylditin (45 mmol), an aryl iodide (30 mmol), and $Pd(PPh_3)_4$ (0.3 mmol) in toluene (60 cm^3) was heated at 60 °C for 72 h under argon. After evaporation to remove the solvent, the residue was washed with aqueous potassium fluoride to remove tributyltin iodide. The organic layer was extracted with benzene and dried over sodium sulfate. Purification was performed by column chromatography (Silica gel: hexane as elutant). The results are shown in Table.

Products. Products were identified by their spectroscopic data and elemental analyses recorded here. *p*-Nitrophenyltributyltin. IR (neat) 1521, 1350 (NO_2), and 870 cm^{-1} (C–C). ^1H NMR (CCl_4) $\delta=0.45$—2.05 (27H, m), and 7.55, 8.12 (4H, ABq, $J=8$ Hz). Found: C, 52.49; H, 7.85; N, 3.27%. Calcd for $C_{18}H_{31}NO_2Sn$: C, 52.46; H, 7.58; N, 3.40%. *m*-Nitrophenyltributyltin. IR (neat) 1521, 1350 (NO_2), and 870 cm^{-1} (C–N). ^1H NMR (CCl_4) $\delta=0.45$—2.05 (27H, m), and 7.30—8.20 (4H, m). Found: C, 52.54; H, 7.63; N, 2.98%. Calcd for $C_{18}H_{31}NO_2Sn$: C, 52.46; H, 7.58; N, 3.40%. *o*-Nitrophenyltributyltin. IR (neat) 1520, 1340 (NO_2), and 855 cm^{-1} (C–N). ^1H NMR (CCl_4) $\delta=0.45$—2.05 (27H, m), and 7.35—7.85, 8.20—8.55 (4H, m). Found: C, 53.10; H, 7.88; N, 3.45%. Calcd for $C_{18}H_{31}NO_2Sn$: C, 52.46; H, 7.58; N, 3.40%. *p*-Acetylphenyltributyltin. IR (neat) 1690, 1275 cm^{-1} (C=O). ^1H NMR (CCl_4) $\delta=0.45$—2.05 (27H, m), 2.53 (3H, s), and 7.47, 7.71 (4H, ABq, $J=6$ Hz) Found: C, 58.08; H, 8.38%. Calcd for $C_{20}H_{34}OSn$: C, 58.71; H, 8.38%. *p*-Cyanophenyltributyltin. IR (neat) 2240 cm^{-1} (C≡N). ^1H NMR (CCl_4) $\delta=0.45$—2.05 (27H, m), and 7.17—7.78 (4H, m). Found: C, 57.96; H, 7.98; N, 3.57%. Calcd for $C_{19}H_{31}NSn$: C, 58.19; H, 7.97; N, 3.57%.

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