One-Pot Palladium-Catalyzed Cross-Coupling Reaction of Aryl Iodides with Stannylarsanes and Stannylstibanes

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Experimental Section

General Methods: Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument with a flame ionisation detector, a Hewlett-Packard 3396 Series III integrator, an one of the following columns: HP1 5 m x 0.53 mm column, and a DB-1, 30 m x 0.17 mm column. ^1H NMR (200.13 MHz) and ^{13}C NMR (50.32 MHz) were conducted on a Bruker AC 200 spectrometer in CDCl_3 as solvent. GC/MS analyses were carried out on a Shimadzu GC/MS QP 5050 spectrometer equipped with a DB-5, 30 m x 0.18 mm ID column.

Materials: Ph_3As , Ph_3Sb , $n\text{-Bu}_3\text{SnCl}$, the palladium catalysts $(\text{PPh}_3)_2\text{PdCl}_2$ and $(\text{PPh}_3)_4\text{Pd}$ and the iodoarenes were commercially available and used as received from the supplier. Toluene and THF were distilled under nitrogen from sodium/benzophenone.

General Procedure for Preparation of Aryldiphenylarsanes and Stibanes from Aryl Iodides. The following procedure is representative of all these reactions. Ammonia (300 mL), previously dried over Na metal, was distilled into a 500-mL three-neck round-bottom flask equipped with a cold finger condenser and a magnetic stirrer. To the ammonia were added Ph_3As (1 mmol) and then Na metal (2 mmol) in small pieces. The addition of Na metal continued until the blue solution from solvated electrons in excess remained for 20 minutes before it became orange-brown and no more solid was present. To this solution was added $t\text{-BuOH}$ to decolorize and then one additional mmol to neutralize the amide ions formed. After that, Ph_2As^- anion was ready for use (clear orange solution). $n\text{-Bu}_3\text{SnCl}$ (1 mmol) was added slowly, the mixture was stirred for 5 minutes and then ammonia was allowed to evaporate. Evaporation left a solid white residue, which was dissolved in dry toluene (30 mL). In the Schlenk tube which contained $(\text{PPh}_3)_2\text{PdCl}_2$ (0.015 mmol) and which was evacuated and filled with nitrogen three times, the above solution was introduced via canula and syringe. Then 1-iodonaphthalene (0.8 mmol) and toluene (5 mL) were added. When the $n\text{-Bu}_3\text{SnAsPh}_2$ solution was introduced, the reaction mixture turned deep brown. The reaction mixture was heated for 24 hours in an oil bath at 80°C . To the cool reaction mixture, water was added and then extracted three times with dichloromethane (30 mL each). After drying with anhydrous MgSO_4 , the products were quantified by GLC using the internal standard method. Naphthalen-1-yl-diphenyl-arsane was purified by silica-gel column chromatography (hexanes-ethyl acetate) to give a white solid mp $105\text{--}106^\circ\text{C}$ (lit.^{20a} mp $105.5\text{--}106.5^\circ\text{C}$). ^1H NMR and ^{13}C NMR data of the products are shown below.

Naphthalen-1-yl-diphenyl-arsane

Naphtalen-1-yl-diphenyl-stibane

(4-Methoxyphenyl)diphenyl-arsane

(4-Chlorophenyl)diphenyl-arsane

(4-Methoxyphenyl)diphenyl-stibane

(4-Chlorophenyl)diphenyl-stibane