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A Simple and Highly Efficient Preparation of Arylstannane via Sonochemical Barbier Reaction

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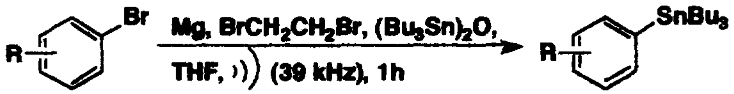
Abstract: Arylstannane is produced by a reaction of aryl bromide, magnesium powder, 1,2-dibromoethane and bis(tributyltin)oxide via sonochemical Barbier-type reaction in a commercial ultrasonic cleaning bath (39 kHz).

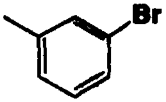
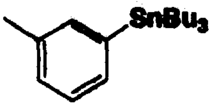
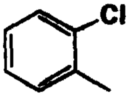
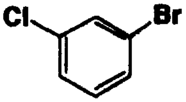
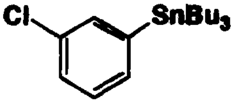
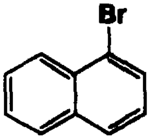
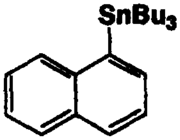
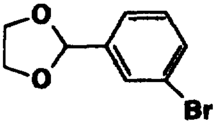
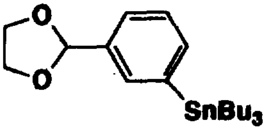
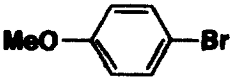
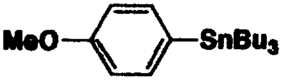
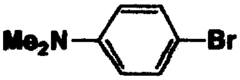
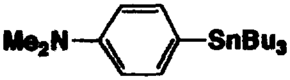
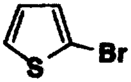
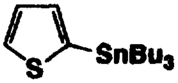
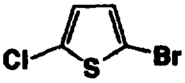
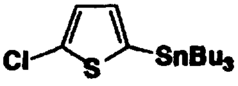
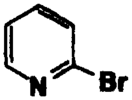
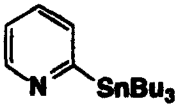
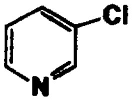
Palladium-catalyzed cross-coupling of organostannanes with organic electrophiles, known as the Stille reaction, has emerged as one of the premier methods for the creation of new carbon-carbon bonds.[1-3] Its scope, functional group compatibility, and stereospecificity are often complementary to those of more conventional anionic processes based on stannyl transmetallation.[4-8] The creation of a tin-carbon bond from simple organotin reagents is a prerequisite for further transformation for use in various applications of organic synthesis. Arylstannanes have been extensively accessed in organic synthesis and are normally prepared by the reaction of the appropriate aryl halide with stannyl chloride. Arylstannane is typically prepared by the reaction of transmetallated aryl halide (Aryl-Metal, Metal = Li, Na, Mg) and R_3SnCl (R = Me, Bu).[9-12] In many cases, side reactions are produced and the yields of the expected products are low. Herewith, we wish to report the novel synthesis of arylstannane via sonochemical Barbier reaction (Scheme1).

Scheme 1



The typical procedure for the preparation of arylstannane from the corresponding aryl bromide is as follows: A solution of aryl bromide (1 mmol), magnesium powder (2.3 mmol), 1,2-dibromoethane (1.1 mmol), and bis(tributyltin)oxide (1 mmol) in anhydrous THF (4 mL) is sonicated for one hour in a commercial ultrasonic cleaning bath (Crest 575-D, 39 kHz) at around 45 °C. After the reaction is complete (monitored by TLC), 15 mL of water is added and extracted with ethyl acetate (3 x 10 mL). The organic layer is collected, washed with brine (15 mL), dried with $MgSO_4$ (Na_2SO_4 for Entries 8-10), filtered, and the organic solvent removed under reduced pressure. Further purification is achieved on a flash chromatograph with silica gel (or aluminum oxide, neutral) and ethyl acetate/hexane. A series of aryl halides are sonicated for one hour and the results are shown in Table 1.

Table 1. Synthesis of arylstannanes

Entry	Substrate	Product	Yield[a]
1			85%[b] 95%
2			N.R.[c]
3			86%[b] 94%
4			N.R.[d] 90%
5			N.R.[d] 80%
6			N.R.[d] 85%
7			N.R.[d] 40%
8			86%[b]
9			80%[b]
10			N.R.[d] 65%
11			N.R.[c]

(a) The yields were determined after chromatographic purification.
(b) In the absence of 1,2-dibromoethane.
(c) In the presence of 1,2-dibromoethane, the starting material was recovered.
(d) In the absence of 1,2-dibromoethane, the starting material was recovered.

It has been known that the Barbier-type reaction can be generated and improved under ultrasound.[13,14] Thus, we first investigated this sonochemical Barbier reaction by using Bu_3SnCl as an electrophile. A solution of Mg, aryl bromide, and Bu_3SnCl in dry THF was sonicated for 30 minutes. The ditin (Bu_3Sn-$SnBu_3$, yield = ~40%) instead of the expected product was created under this reaction condition. Other metals (Zn[15-18], Zn/Cu[19-22], Mg-Cu[23]) were then investigated and either the starting material or the ditin formation was observed. Hypothesizing that if $(Bu_3Sn)_2O$ was used to replace Bu_3SnCl, we might be able to prevent dimerization of Bu_3SnCl, a new test was undertaken. A solution of bromotoluene (Entry 1), Mg and $(Bu_3Sn)_2O$ in dry THF was sonicated for 60 minutes and an 85% yield of stannyltoluene was indeed produced. Despite success under this condition, other aryl bromides (Entries 4-7,10) were resistant to these reaction conditions.

While Grignard reagents of aryl halides and vinyl halides are difficult to form, addition of activators has been developed to enable the preparation of these difficult-to-access Grignard reagents.[24] Thus, a few activators (e.g., iodine, 1,2-dibromoethane) for magnesium were introduced to investigate the formation of arylstannane from aryl halide. It was found that in the presence of 1,2-dibromoethane, aryl bromides were converted to their corresponding arylstannanes in high yields, whereas the aryl chlorides (Entries 2,11) were resistant to this reaction conditions. It is worthwhile to note that the reflux condition can not produce arylstannane in the absence of 1,2-dibromoethane.[25] In the presence of 1,2-dibromoethane, the reflux condition can produce arylstannane but at a lower yield (typically 10% lower). High chemoselectivity between the bromide and chloride can be achieved (Entries 3, 9) and heterocyclic stannyl compounds can also be produced under the reaction conditions (Entries 8-10).

It has been proposed that $MgBr_2$ is generated *in situ* when Mg reacts with 1,2-dibromoethane.[26,27] Therefore, in our test, Mg + $MgBr_2$ was introduced to replace the Mg + $BrCH_2CH_2Br$ system for investigation under ultrasonic condition. A solution of *p*-bromomethoxybenzene (Entry 6, 1 mmol), Mg (2.3 mmol), $MgBr_2$ (1.1 mmol) and $(Bu_3Sn)_2O$ (1 mmol) in 4 mL THF was sonicated for 60 minutes and a 46% yield of arylstannane was produced. The *in situ* generated $MgBr_2$ seems to produce arylstannane at a higher yield. It is also worthwhile to note that a small amount of 1,2-dibromoethane is adequate enough for the arylstannane formation but with a lower yield. A solution of bromobenzene (Entry 5, 1 mmol), Mg (1.4 mmol), $BrCH_2CH_2Br$ (0.2 mmol) and $(Bu_3Sn)_2O$ (1 mmol) in 4 mL THF was sonicated for 60 minutes and a 64% yield of stannylbenzene was produced.

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