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Novel Access to Organostannane Compounds under Ultrasound Irradiation

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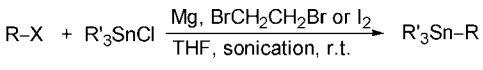
A simple and efficient procedure has been developed for the synthesis of organostannane compounds by one-pot reaction of stannane halides, magnesium turnings and organic halides in the presence of 1,2-dibromoethane under ultrasound irradiation.

Keywords organostannane, one-pot reaction, ultrasound irradiation

Organostannanes are being found increasing application in organic synthesis[1] and there is a continuous interest in methods of preparation of these compounds. Usually organostannanes were synthesized by the reactions of organolithium or organomagnesium derivatives with trialkyltin halides[2] or of stanyl metal R_3SnM (M= Li, Na, Cu) with appropriate electrophiles (organic halides).[3] Another important method is the radical-induced[4] or Pd-promoted[5] addition of tin hydrides to unsaturated systems (*e.g.*, alkynes, alkenes). Such reactions were typically carried out in anhydrous organic solvents. In many cases, these reactions are accompanied with side reactions resulting in low yields of the desired products. Lee[6] described a more practical method which produced organostannanes by a sonochemical reaction of the corresponding bromides, magnesium, 1,2-dibromoethane and bis(tributyltin) oxide. However, Lee's procedure gave good yields only in anhydrous THF. Concerning our interest in the synthesis and chemistry of organostannanes,[7,8] we reported herein an improved procedure for the synthesis of organostannanes (aryl, alkyl, allyl and vinyl) compounds by one-pot reaction of stannane halides, magnesium turnings and organic halides (Br, Cl, I) in the presence of 1,2-dibromoethane (or a piece of I_2) under ultrasonic conditions[9] (Scheme 1). This method provided various kinds of organostannanes in almost quantitative yield from the corresponding organic halides and chlorotriallylstannane.

Scheme 1



R = aryl, allyl, alkyl, vinyl; R'=Bu, Me; X=Cl, Br, I

A wide range of stannane compounds was subjected to this procedure to produce the corresponding products in quite high yield. Gram-scale reactions with 0.1—10.0 g of stannane halide were also carried out to give analogously good yields of the corresponding products. The results are presented in Table 1.

Table 1 Preparation of organostannane compounds from organic halides

Entry	Organic halide	R′	Organostannane	Yield/ %
1	*s*-BuBr	Bu	*s*-$BuSnBu_3$ (**1**)	96
2	$Br(CH_2)_6Br$	Bu	$Bu_3Sn(CH_2)_6SnBu_3$ (**2**)	95
3	PhBr	Bu	$PhSnBu_3$ (**3**)	95
4	*p*-$MeOC_6H_4Br$	Bu	*p*-$MeOC_6H_4SnBu_3$ (**4**)	95
5	$PhCH_2Cl$	Bu	$PhCH_2SnBu_3$ (**5**)	95
6	$PhCH_2Cl$	Me	$PhCH_2SnMe_3$ (**6**)	96
7	$PhCH(CH_3)I$	Bu	$PhCH(CH_3)SnBu_3$ (**7**)	95
8	Ph_2CHI	Bu	$Ph_2CHSnBu_3$ (**8**)	95
9	*o*-$C_6H_4(CH_2I)_2$	Bu	*o*-$C_6H_4(CH_2SnBu_3)_2$ (**9**)	95
10	*E*-PhCH=CHBr	Bu	*E*-PhCH=$CHSnBu_3$ (**10**)	trace
11	CH_2=$CHCH_2Cl$	Bu	CH_2=$CHCH_2SnBu_3$ (**11**)	95
12	Bu_3SnCl	Bu	Bu_3Sn-$SnBu_3$ (**12**)	95
13	CH_2=CHBr	Bu	CH_2=$CHSnBu_3$ (**13**)	90

Apparently, higher yields and shorter time were observed when aryl, allyl and alkyl halides were used in the reaction than those Lee has observed. But unfortunately, almost no reaction happened when alkenyl halides (except vinyl bromide, Entry 13) were used (Entry 10). But when $(Bu_3Sn)_2O$ was replaced with Bu_3SnCl, a series of alkenylstannanes were prepared successfully

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by Lee. Finally, treatment of Bu_3SnCl with Mg in THF by ultrasound irradiation affords $Bu_3Sn\text{-}SnBu_3$ (Entry 12), while in the presence of allyl or alkyl halides no any distannane was detected.

Conclusion

As seen, this methodology can accommodate a variety of organic functional halides, the yields are nearly quantitative. It should be noted that (a) the quality of the reagents is not critical (solvent or halides) and they do not need to be purified before use, and (b) the use of 1,2-dibromoethane or I_2 is not necessary but usually it can increase the yield.

Experimental

The following procedure is representative: A flask containing 10 mL of THF, 480 mg (20 mmol) of magnesium turnings, 0.1 mL of 1,2-dibromoethane, 3.25 g (10 mmol) of tributylstannane chloride and 10 mmol of organic functional halide was plunged into a commercial ultrasonic cleaning bath (KQ-250, working frequency: 40 kHz) and sonicated for 0.5 h. The mixture was treated by the usual way to give the corresponding organostannane products in almost quantitative yield.

2-Methylpropyltributylstannane (1): IR (film) *v*: 2957, 1656, 1465 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.90—1.86 (m, 1H), 1.52—1.44 (m, 6H), 1.41—1.24 (m, 6H), 0.94—0.68 (m, 23H).

1,6-Bis(tributylstannane)hexane (2): IR (film) *v*: 2900, 1616, 1435 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.60—1.40 (m, 14H), 1.38—1.13 (m, 18H), 1.04—0.68 (m, 34H).

Phenyltributylstannane (3): IR (film) *v*: 2950, 1644 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.56—7.36 (m, 5H), 1.64—1.58 (m, 6H), 1.52—1.36 (m, 6H), 1.21 (t, J=7.6 Hz, 9H), 0.97 (t, J=7.6 Hz, 6H).

4-Methoxyphenyltributylstannane (4): IR (film) *v*: 2950, 1644 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.50—7.26 (m, 2H), 6.92 (d, J=8.6 Hz, 2H), 3.82 (s, 3H), 1.71—1.44 (m, 6H), 1.41—1.25 (m, 6H), 1.21—0.97 (m, 15H).

Benzyltributylstannane (5): IR (film) *v*: 3020, 2957, 1600, 1465 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.16 (t, J=7.6 Hz, 2H), 7.03—6.98 (m, 3H), 2.32 (s, 2H), 1.54—1.45 (m, 6H), 1.41—1.36 (m, 6H), 0.92—0.82 (m, 15H).

Benzyltrimethylstannane (6): IR (film) *v*: 3012, 2870, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.10—7.06 (m, 2H), 7.02—6.98 (m, 3H), 2.20 (s, 2H), 0.02 (s, 9H).

(α-Methylbenzyl)tributylstannane (7): IR (film) *v*: 2957 (s), 2928 (s), 2871 (s), 2856 (s), 1600 (m), 1492 (m), 1457 (m), 1376 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.23 (t, J=7.6 Hz, 2H), 7.06—7.02 (m, 3H), 2.73 (q, J=7.6 Hz, 1H), 1.60 (d, J=7.6 Hz, 3H), 1.44—1.24 (m, 15H), 0.91—0.78 (m, 12H).

(1,1-Diphenylmethyl)tributylstannane (8): IR (film) *v*: 2960, 1940, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.28—7.25 (m, 4H), 7.21—7.19 (m, 4H), 7.10 (t, J=7.3 Hz, 2H), 4.07 (s, 1H), 1.40—1.32 (m, 6H), 1.27—1.20 (m, 6H), 0.87—0.84 (m, 15H).

1,2-Bis(tributylstannanylmethyl)benzene (9): IR (film) *v*: 3070, 1910, 1010, 945 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.94—6.90 (m, 2H), 6.86—6.84 (m, 2H), 2.19 (s, 4H), 1.50—1.42 (m, 12H), 1.32—1.26 (m, 12H), 0.92—0.83 (m, 30H).

2-Propenyltributylstannane (11): IR (film) *v*: 3080, 2910, 1620, 880 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 5.94—5.90 (m, 1H), 4.76 (d, J=18.0 Hz, 1H), 4.64 (d, J=10.0 Hz, 1H), 1.78 (d, J=8.7 Hz, 2H), 1.54—1.44 (m, 6H), 1.37—1.26 (m, 6H), 0.99—0.83 (m, 15H).

Hexabutyldistannane (12): IR (film) *v*: 3030, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.45—1.37 (m, 12H), 1.27—1.19 (m, 12H), 0.92—0.80 (m, 30H).

Ethenyltributylstannane (13): IR (film) *v*: 3070, 1910, 1010, 945 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.53—6.41 (dd, J=21.0, 14.0 Hz, 1H), 6.18—6.12 (dd, J=14.0, 3.8 Hz, 1H), 5.70—5.62 (dd, J=21.0, 3.8 Hz, 1H), 1.54—1.42 (m, 6H), 1.33—1.26 (m, 12H), 0.92—0.88 (m, 9H).

References

1 For reviews see:
(a) Stille, J. K. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(b) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1.
(c) Duncton, M. A. J.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1235.
(d) Zhang, S. M.; Li, H.; Zheng, X. C.; Li, B. Q.; Wu, S. H.; Huang, W. P.; Liu, Z. G.; Feng, Y. *Chin. J. Org. Chem.* **2002**, *22*, 603 (in Chinese).
(e) Bian, Y. J.; Li, J. T.; Li, T. S. *Chin. J. Org. Chem.* **2002**, *22*, 227 (in Chinese).

2 (a) Iddon, B.; Lim, B. L. *J. Chem. Soc., Perkin Trans. 1* **1983**, 271.
(b) Wursthorn, K. R.; Kuivila, H. G. *J. Organomet. Chem.* **1977**, *140*, 29.

3 Gawley, R. E. *Tetrahedron Lett.* **1999**, *40*, 4297.

4 Ferezou, J. P.; Julia, M.; Li, Y.; Liu, L. W.; Pancrazi, A. *Synlett.* **1991**, 53.

5 Zhang, H. X.; Guibe, F. Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.

6 Lee, A. S. Y.; Dai, W. C. *Tetrahedron* **1997**, *53*, 859.

7 (a) Peng, L. Z.; Zhang, F. Z.; Mei, T. S.; Zhang, T.; Li. Y. L. *Tetrahedron Lett.* **2003**, *44*, 5921.
(b) Zhang, F. Z.; Peng, L. Z.; Mei, T. S.; Zhang, T.; Li. Y. L. *Synth. Commun.* **2003**, *33*, 3771.

8 Peng, L. Z.; Mei, T. S.; Zhang, T.; Li. Y. L. *Chin. Chem. Lett.* **2003**, 341.

9 David-Quillot, F.; Lunot, S.; Marsacq, D.; Duchene, A. *Tetrahedron Lett.* **2000**, *41*, 4905.

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