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Synthesis of asymmetrical aryl–tin compounds by cleavage of alkyl–tin bonds with sodium metal in liquid ammonia followed by $S_{RN}1$ reactions with chloroarenes

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Abstract

One methyl–tin bond was selectively cleaved from aryltrimethyltin compounds by sodium metal in liquid ammonia. The triorganylstannyl anions thus obtained are arylated by chloroarenes by means of photostimulated $S_{RN}1$ reactions. Such reactions can be repeated to replace all methyl groups by different aryl groups. The one-pot synthesis of asymmetric triarylmethyltin compounds can be achieved from trimethyltin chloride.

Keywords: Tin; Nucleophilic substitution; Electron transfer; $S_{RN}1$

1. Introduction

There are several examples of synthesis of racemic [1,2] and optical active organotin compounds (by diastereomeric separation [3,4] or asymmetric induction [5–7]) in the chemical literature. In most cases, asymmetrical tetraalkyl or mixed alkylaryltins were obtained, while asymmetrical tetraaryltins have not been reported. The main way to achieve this kind of compound consists of an electrophilic cleavage of a C–Sn bond with halogens, followed by a reaction with a Grignard reagent to make the new C–Sn bond (e.g. Eq. (1)) [4].

$$Ph_3(^iPr)Sn \xrightarrow[Cl_3CH]{I_2} \underset{(83\%)}{Ph_2(^iPr)SnI} \xrightarrow[Et_2O]{MeI/Mg} \underset{(82\%)}{Ph_2(^iPr)SnMe} \quad (1)$$

The selectivity observed for the electrophilic cleavage of C–Sn bonds is as follows: *o*-tolyl > *p*-tolyl > phenyl > benzyl > vinyl > methyl > ethyl > propyl > butyl, etc. [8]. These reactions can be repeated successively, leading to asymmetrical organotin derivatives. All of these reactions must be performed stepwise, isolating each intermediate product.

We have previously described the photostimulated reactions of sodium trimethylstannyl and sodium triphenylstannyl as nucleophiles towards aryl halides in liquid ammonia, which give very good to excellent yields (70–100%) of nucleophilic substitution products with a number of chloroarenes (Eq. 2) [9], i.e.

$$ArCl + R_3Sn^- \xrightarrow[S_{RN}1]{h\nu, NH_3} R_3SnAr + Cl^- \quad (2)$$

R = Me, Ph

Ar = *p*-tolyl, *p*-anisyl, 1-naphtyl, 2-quinolyl

The fact that there is no reaction in the dark, but only under irradiation, and that the photostimulated reactions were inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions, strongly suggests that these reactions occur by the $S_{RN}1$ mechanism [9,10], which is a well-known process for substitution on a non-activated adequately substituted substrate [11]. This mechanism is depicted for haloarenes in Eqs. (3)–(7). On the whole, the propagation steps (Eqs. (4)–(6)) indicate a nucleophilic substitution in which radicals and radical anions are intermediates. This chain process requires an initiation step (Eq. (3)). In a few systems,

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spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed, and the resulting radical anion $(ArX)^{\cdot-}$ initiates the chain propagation steps. When the ET reaction does not occur spontaneously, it can be induced by light stimulation [11]. The termination steps (Eq. (7)) are not important for a number of systems, including those in which the nucleophile is a triorganostannyl anion.

$$ArX + Nu^- \xrightarrow{h\nu} (ArX)^{\cdot-} + Nu^{\cdot} \quad (3)$$

$$(ArX)^{\cdot-} \longrightarrow Ar^{\cdot} + X^- \quad (4)$$

$$Ar^{\cdot} + Nu^- \longrightarrow (ArNu)^{\cdot-} \quad (5)$$

$$(ArNu)^{\cdot-} + ArX \longrightarrow ArNu + (ArX)^{\cdot-} \quad (6)$$

$$Ar^{\cdot} \xrightarrow{e^-} Ar^- \xrightarrow{SH} ArH \quad (7)$$

The $S_{RN}1$ reactions using sodium trimethylstannyl as nucleophile (Eq. (2)) would be used to synthesize asymmetrical tetraaryltins if an asymmetrical nucleophile were generated from the substitution product Me_3SnAr. Then, this new nucleophile could be arylated by an $S_{RN}1$ reaction with another chloroarene, leading to the replacement of a methyl group by an aryl group (Eq. (8)).

$$Me_3SnAr \xrightarrow[NH_3]{Na} ArMe_2Sn^- \xrightarrow[S_{RN}1]{Ar'Cl} ArMe_2SnAr' \quad (8)$$

The present work describes this kind of reaction affording asymmetrical aryl–tin compounds.

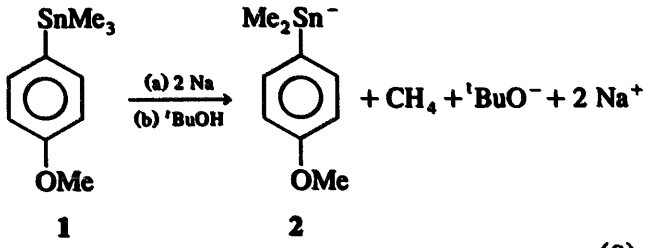
2. Results and discussion

We found that a Sn–Me bond in *p*-anisyltrimethyltin (1) is cleaved with Na metal in liquid ammonia to give the nucleophile 2, consistent with the bond dissociation energy difference between tin–phenyl (347 kJ mol^{-1}) [12] and tin–methyl (259–272 kJ mol^{-1}) [12,13] bonds. No products formed by fragmentation of the *p*-anisyl–Sn bond were observed (Eq. (9)) [14].

Table 1
Arylation reactions of asymmetrical trioganyltin nucleophiles in liquid ammonia [a]

Expt.	Starting material ($\times 10^{-3}$ M)	Reaction conditions [b] ($\times 10^{-3}$)	Cl^- (%)	Products (%)
1	*p*-$AnMe_3Sn$ (9.0)	Na, ^tBuOH, 3 (8.1), hν-60′	100	4 (≈ 100) [c]
2	Me_3SnCl (10.8)	(a) Na, 5 (9.9), hν-60′	91 [e]	4 (89) [c]
		(b) Na, ^tBuOH, 3 (11.0), hν-60′		(63) [d]
3	*p*-An(*p*-To)Me_2Sn (5.6)	Na, ^tBuOH, ClPh (5.0), hν-60′	– [f]	6 (31) [d]
				7 [f], 8 [f]
4	Me_3SnCl (19.5)	(a) Na, 5 (17.8), hν-60′	87 [g]	6 (47) [c]
		(b) Na, ^tBuOH, 3 (19.6), hν-60′		7 [f]
		(c) Na, ^tBuOH, ClPh (19.5), hν-120′		8 [f]
5	Me_3SnCl (19.6)	(a) Na, 5 (18.1), hν-60′	– [f]	6 (26) [d]
		(b) Na, ^tBuOH, 3 (20.1), hν-60′		7 (37) [d]
		(c) Na, ^tBuOH, ClPh (19.6), hν-120′		8 (9) [d]
6	Me_3SnCl (19.5)	(a) Na, ClPh (17.8), hν-40′	– [f]	6 (33) [e]
		(b) Na, ^tBuOH, 3 (19.6), hν-60′		4 (50) [e]
		(c) Na, ^tBuOH, 5 (19.6), hν-90′		8 (15) [e]
7	$^pAn(^pTo)PhMeSn$ (7.0)	Na, ^tBuOH, ^pClBiPh (7.6), hν-140′	– [f]	9 (25) [e]
				10 (31) [e]
				11 (24) [e]
				12 (11) [e]
8 [h]	Me_3SnCl (20.0)	(a) Na, 5 (20.0), hν-60′	– [f]	8 (66) [i,j]
		(b) Na, ^tBuOH, ClPh (22), hν-60′		
9 [h]	Me_3SnCl (21.0)	(a) Na, 3 (20.0), hν-60′	– [f]	7 (63) [i,k]
		(b) Na, ^tBuOH, ClPh (22), hν-60′		

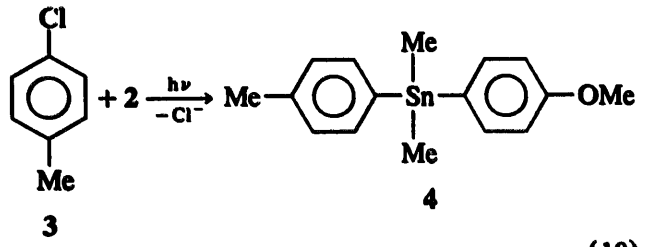
[a] Reactions were carried out in about 250 ml of liquid ammonia unless otherwise indicated.
[b] Sodium metal and ^tBuOH were respectively used in about 15% excess and stoichiometric quantity with respect to the starting material or intermediate products in all the reactions. Irradiation was conducted in a four 250-W lamp reactor (Expts. 1–6) and in a two 400-W lamp reactor (Expts. 7–9).
[c] Determined by GLC.
[d] Isolated yield (radial TLC).
[e] Obtained by subtraction of chlorides from the starting material.
[f] Not quantified.
[g] Calculated for step (c), with the assumption of total dehalogenation in steps (a) and (b).
[h] Reaction carried out in about 500 ml of liquid ammonia.
[i] Isolated yield (vacuum-distilled using a Kugelrohr apparatus).
[j] $PhMe_3Sn$ was also isolated (< 5%).
[k] $PhMe_3Sn$ was also isolated (12%).



1 2

(9)

After neutralization of the generated amide ions with *tert*-butyl alcohol, the nucleophile **2** was allowed to react with *p*-chlorotoluene **3** under photostimulation by the $S_{RN}1$ mechanism to give (*p*-anisyl)dimethyl(*p*-tolyl)tin (**4**) in almost quantitative yields (Eq. (10)) (Table 1, Expt. 1).

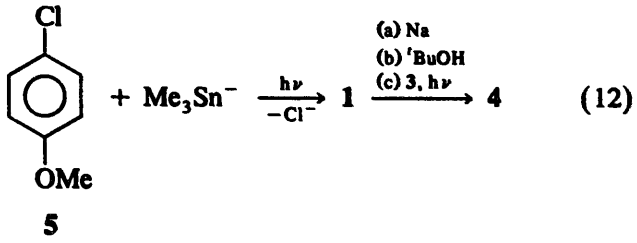


3 4

(10)

The arylated product **4** was also obtained by a one-pot reaction starting from trimethyltin chloride. The reaction of trimethyltin chloride with Na metal in liquid ammonia gives Me_3Sn^- ions (Eq. (11)) [9]. The photostimulated reaction of this nucleophile with *p*-chloroanisole (**5**) gave the substitution product **1**, which was not isolated, and it was treated with Na metal to give the nucleophile **2**, which by photostimulated reaction with **3** gave the product **4** in very good yields in a one-pot reaction (89% overall yield) (Eqs. (11)–(12) and Table 1, Expt. 2).

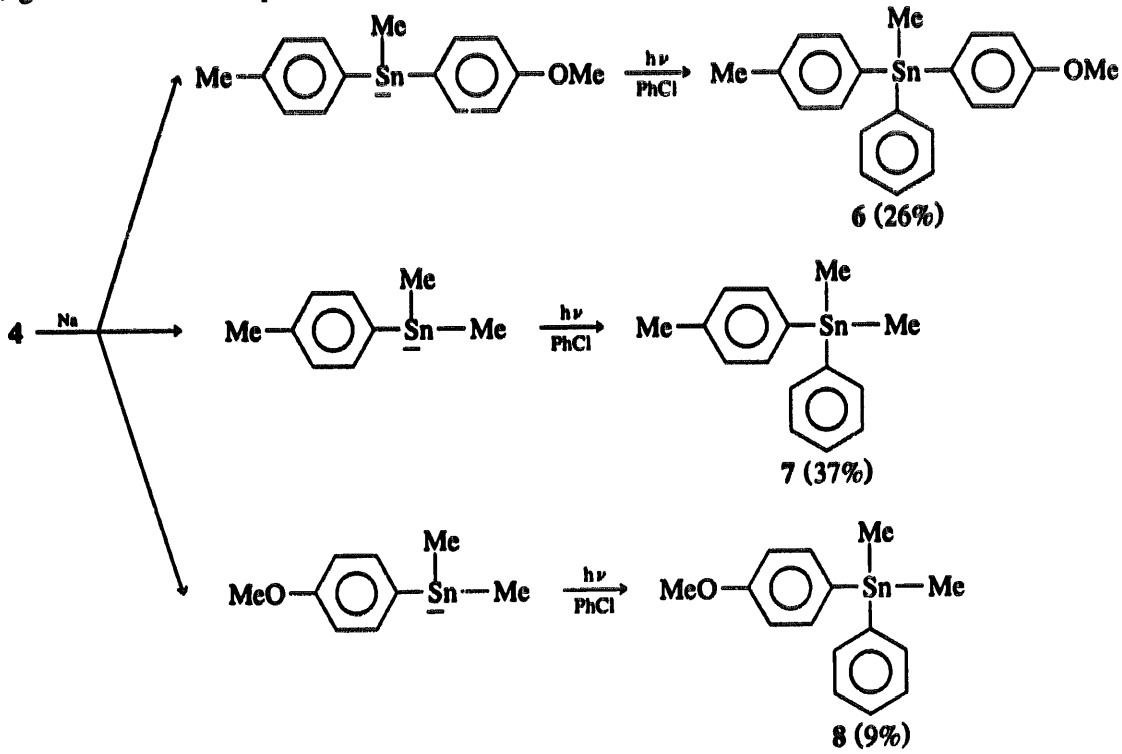
$$Me_3SnCl + 2Na \longrightarrow Me_3Sn^- + Cl^- + 2Na^+ \qquad (11)$$



5 (12)

When **4** was cleaved by Na metal in liquid ammonia, a decrease of the selectivity was observed, affording a mixture of products after the photostimulated reaction with chlorobenzene under $S_{RN}1$ conditions (Table 1, Expt. 3). The product distribution of the corresponding one-pot reaction starting from trimethyltin chloride is shown in Scheme 1 (isolated yields) (Table 1, Expts. 4 and 5).

In order to see if the selectivity of this reaction could be increased, the one-pot reaction was performed with inversion of the addition order of the chloroarenes, i.e. the photostimulation reaction of Me_3Sn^- ions with chlorobenzene and then, after treatment with Na metal, **3** was added under irradiation, followed by a new treatment of Na metal, and **5** was afterwards added,



Scheme 1.

obtaining a similar product distribution (Eq. (13) and Table 1, Expt. 6).

$$Me_3SnCl \xrightarrow[\text{(c) Na metal, }^t\text{BuOH; (d) 3, h}\nu \text{ (e) Na metal, }^t\text{BuOH; (f) 5, h}\nu]{\text{(a) Na metal; (b) PhCl, h}\nu} 6\ (33\%) + 4\ (50\%) + 8\ (15\%) \quad (13)$$

To obtain an asymmetrical tetraaryltin, the triarylmethyltin 6 was treated with Na metal, and then with *p*-chlorobiphenyl. The completely asymmetrical tetraaryltin (*p*-anisyl)(*p*-biphenyl)phenyl(*p*-tolyl)tin (9) was obtained in 25% yield, along with the other three possible products 10–12 (Table 1, Expt. 7).

In order to learn the selectivity of the bond fragmentation, we studied the reaction of methyltriphenyltin (13) with Na metal in liquid ammonia, in which three phenyl–tin bonds compete with one methyl–tin bond. In this reaction, followed by the addition of benzylchloride to trap the ions formed, 13 gave benzyltriphenyltin (14), benzylmethyldiphenyltin (15) and a small amount of benzyldimethylphenyltin (16) (Eq. (14) and Table 2, Expt. 3).

$$\underset{13}{Ph_3SnMe} \xrightarrow[\text{(b) }^t\text{BuOH}]{\text{(a) Na}} \xrightarrow{PhCH_2Cl} \underset{14}{Ph_3SnCH_2Ph} + \underset{15}{Ph_2(Me)SnCH_2Ph} + \underset{16}{Ph(PhCH_2)SnMe_2} \quad (14)$$

These results suggest that the reaction of 13 with Na metal in liquid ammonia gave methyl radicals and phenyl radicals by fragmentation of the Me–Sn (Eq. (15a)) and Ph–Sn bonds (Eq. (15b)) respectively, with a Sn–Me/Sn–Ph cleavage ratio of about 2.9.

$$\underset{13}{Ph_3SnMe} + Na \rightarrow \begin{cases} Ph_3Sn^- + Me^\cdot & (15a) \\ Ph_2MeSn^- + Ph^\cdot & (15b) \end{cases}$$

The fact that the dimethylated tin compound 16 was obtained in about 10% yield suggests that methyl radicals, besides being reduced to methane by reaction with Na metal and liquid ammonia, are also able to react with Ph_2MeSn^- ions to form the dimethylated radical anion 17, which suffers either a Sn–Me bond cleavage to give the starting reactants, or a Sn–Ph bond cleavage to render finally the anion $PhMe_2Sn^-$ (Eq. (16)), which, by quenching with benzylchloride, ultimately gives the product 16. There is precedent in $S_{RN}1$ reactions for the scrambling of products from the reversible formation of radical anions, and fragmentation in other σ bonds [15].

$$Ph_2MeSn^- + Me^\cdot \rightleftharpoons \underset{17}{(Ph_2Me_2Sn)^-} \rightleftharpoons PhMe_2Sn^- + Ph^\cdot \quad (16)$$

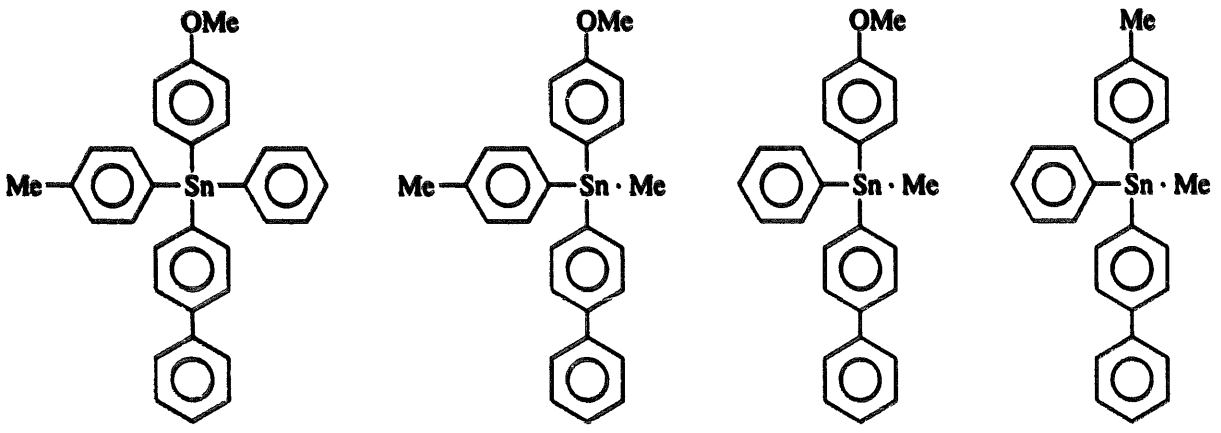
In order to increase the selectivity in the cleavage of 13, reactions using sodium amalgam (3%) or Na metal in liquid ammonia at −78 °C were carried out, but without success.

The degree of cleavage selectivity can be improved by changing the methyl group for other alkyl groups with a lower Sn–C bond dissociation energy. In fact, the cleavage of either *n*-butyltriphenyltin (18) (D(Sn–Bu) = 209 kJ mol^{-1}) [12] or benzyltriphenyltin (14) (D(Sn–CH_2Ph) = 163 kJ mol^{-1}) [16] led exclusively

Table 2
Cleavage reactions of alkyltriphenyltins [a]

Expt.	Ph_3SnR ($\times 10^{-3}$ M)	Trapping reagent RX [b]	Trapped products (% yield) [c]
1	Ph_3SnCH_2Ph (1.0)	IMe	Ph_3SnMe (100)
2	Ph_3SnBu (3.9)	$ClCH_2Ph$	Ph_3SnCH_2Ph (100)
3	Ph_3SnMe (4.1)	$ClCH_2Ph$	Ph_3SnCH_2Ph (49)
			$Ph_2MeSnCH_2Ph$ (41)
			$PhMe_2SnCH_2Ph$ (10)

[a] Reactions carried out in about 250 ml of liquid ammonia. Sodium metal and ^{t}BuOH were respectively used in about 15% excess and stoichiometric quantity with respect to the Ph_3SnR.
[b] 20% in excess.
[c] Determined by NMR.



9 (25%) 10 (31%) 11 (24%) 12 (11%)

Scheme 2.

to Sn–alkyl fragmentation (Eq. (17)) (Table 2, Expts. 1–2). These results suggest that nucleophiles such as tributylstannyl and tribenzylstannyl ions would be more appropriate than trimethylstannyl ions for the reactions of asymmetric synthesis. However, tributyl- and tribenzylstannyl anions could not be prepared in high yields from the corresponding trialkyltin chlorides owing to the low solubility of the starting materials in liquid ammonia. Tributyltin hydride was also tried as a nucleophile precursor, although without success.

$$Ph_3SnR \xrightarrow[(b)\ {}^tBuOH]{(a)\ 2\ Na} Ph_3Sn^- + RH + {}^tBuO^- \quad (100\%)$$

18, R = ^{n}Bu
14, R = $PhCH_2$

(17)

Apparently, the selectivity of fragmentation mainly depends on the dissociation energy difference between Sn–alkyl and Sn–aryl bonds; for example, when alkyl = Bu and CH_2Ph, only the alkyl–tin bond fragments. When such a difference is lower (alkyl = Me), the relative stability of the generated fragments becomes important.

In addition, the one-pot reaction and work-up to obtain (*p*-anisyl)dimethyl(*p*-tolyl)tin (**4**) (Eqs. (11)–(12) and Table 1, Expt. 2) were slightly modified in order to learn the practicality of this method in terms of obtaining diaryldimethyltin compounds in gram quantities. Thus, *p*-anisyldimethylphenyltin (**8**) and dimethylphenyl(*p*-tolyl)tin (**7**) were synthesized in preparative scale (Table 1, Expts. 8–9). The yields of pure products are very good, and the reaction and purification methods can be applied to greater quantities of materials.

Thus, the Na metal cleavage–$S_{RN}1$ reaction in liquid ammonia provides an important route to synthesize asymmetrical organotins in one-pot or consecutive reactions. Work is in progress to discover the scope of this novel synthesis of organotin compounds.

3. Experimental section

3.1. General method

The chloroarenes used as substrates in these reactions were commercially available and utilized as received. Most NMR spectra were recorded on a Bruker FT-200 nuclear magnetic resonance spectrometer; chemical shifts are reported in ppm relative to Me_4Si (TMS). High resolution (HRMS) and mass spectra (MS) were obtained with a Finnigan MAT-90 (The University of Illinois at Chicago, USA), a Finnigan MAT (Dortmund University, Germany), or a Finnigan 3300 f-100 (Universidad Nacional de Córdoba) mass spectrometer.

Elemental analyses were performed at Dortmund University (Germany) and at Galbraith Laboratories Inc. (Knoxville, TN, USA). Gas chromatographic analyses were performed on a Shimadzu GC-8A, Konik 3000-HRGC or Hewlett–Packard 5890 Series II instruments with a flame ionization detector and data systems Shimatzu CR-6A, Konik 825-318 or Hewlett–Packard 3396 Series II, using columns packed with 5% OV17 on Chromosorb G (1.50 m × 3 mm), 3% SE30 on Chromosorb P (0.30 m × 3 mm) or a capillary column HP-1 (methyl silicone, 5 m × 0.53 mm × 2.65 μm). Irradiation was conducted in a reactor equipped with four 250-W or two 400-W lamps with peak emission at 350 nm (Philips Model HPT, water-cooled).

Potentiometric titration of halide ions was performed in a pH meter (Seybold Wien) using an Ag/Ag^+ electrode. TLC plates were precoated with normal silica gel with 254 nm fluorescent indicator (mean pore diameter, 60 Å). The products were isolated by preparative radial thin-layer chromatography (radial TLC), using silica gel 60 PF-254 with calcium sulfate (E. Merck). In general, the solvent system used for both TLC and radial TLC consisted of petroleum ether 100% or petroleum ether/ethyl ether 99.5:0.5 to petroleum ether/ethyl ether 95:5. Melting points were obtained with a Büchi 510 apparatus, and are not corrected.

3.2. Photostimulated reaction of p-anisyldimethylstannyl sodium with p-chlorotoluene in liquid ammonia (Table 1, Expt. 1)

The following procedure is representative of the reactions. Into a three-necked, 500 ml, round-bottomed flask equipped with a cold finger condenser charged with ethanol, a nitrogen inlet and a magnetic stirrer were condensed 250 ml of ammonia previously dried with Na metal under nitrogen [17]. To form *p*-anisyldimethylstannyl sodium (a lemon-yellow solution), *p*-anisyltrimethyltin (2.25 mmol) was added and then Na metal (5.2 mmol, 15% excess) in small pieces, waiting for total decoloration between each addition, and 20–30 min after the last addition (the solution remained blue during this time) ^{t}BuOH (2.25 mmol) was added to neutralize the amide ions formed. *p*-Chlorotoluene (2.0 mmol) dissolved in 1 ml of anhydrous ethyl ether was added to the solution, and the reaction mixture was irradiated for 60 min. The reaction was quenched by adding ammonium nitrate in excess; 50 ml of ethyl ether were added and the ammonia was allowed to evaporate. Water was added, the phases were separated and then the aqueous phase was twice extracted with diethyl ether (50 ml each). The organic phase was dried with sodium sulfate and filtered. The product *p*-anisyldimethyl(*p*-tolyl)tin (**4**) was then determined by GLC with the internal standard method (about 100%, based on *p*-chlorotoluene).

3.3. One-pot synthesis of p-anisyldimethyl(p-tolyl)tin (4) from trimethyltin chloride in liquid ammonia (Table 1, Expt. 2)

The following procedure is representative of these reactions. To 250 ml of dry liquid ammonia treated as before, trimethyltin chloride (2.70 mmol) and Na metal (6.2 mmol, 15% excess) were added to form trimethylstannyl sodium [9]. To this solution *p*-chloroanisole (2.5 mmol, dissolved in 1 ml of anhydrous ethyl ether) was added and the reaction mixture was irradiated for 60 min. The equipment was taken from the photochemical reactor, and Na metal (5.7 mmol, 15% excess) and then ^{t}BuOH (2.5 mmol) were added to the solution to form the second nucleophile. *p*-Chlorotoluene (2.75 mmol, 10% excess) was added with a syringe (without solvent) and the reaction mixture was irradiated for 60 min, with the formation of a white solid. The reaction was quenched and treated as before. The product *p*-anisyldimethyl(*p*-tolyl)tin (4) was determined by GLC in 89% yield (based on *p*-chloroanisole), and it was isolated as pure product in 63% yield (544.5 mg) using radial TLC.

3.4. One-pot synthesis (preparative scale) of p-anisyldimethylphenyltin (8) from trimethyltin chloride in liquid ammonia (Table 1, Expt. 8)

The reaction was similar to the previous one, but was carried out in a 1 litre round-bottomed flask, containing about 500 ml of liquid ammonia. Owing to the greater quantities of reactants, the times needed for nucleophile formation rose from 30–45 min to about 90 min. Once the reaction was finished, the dried organic extract was distilled under vacuum using a Kugelrohr apparatus. The product 8 distilled at 160–170 °C (0.5 mmHg) and gave 2.2 g (66% yield) of pure product (97%, CGL). Trimethylphenyltin was obtained as by-product (less than 5% yield), and distilled before the compound 8, at 77 °C (0.4 mmHg). Column chromatography seems to be a purification method unsuitable for these anisyltin derivatives, since they decompose on long contact with silica gel.

p-Anisyltrimethyltin (1). Synthesized by the photostimulated reaction of $NaSnMe_3$ and *p*-chloroanisol in liquid ammonia by the $S_{RN}1$ mechanism (100% yield (CGL)). Purified by radial TLC (eluted with petroleum ether, 30–60 °C), colorless liquid [18]. ^{1}H NMR ($CDCl_3$, 80.13 MHz): δ 0.26 (s, 9H, ^2J(SnCH) = 53.7 Hz), 3.80 (s, 3H), 6.92 and 7.41 (AA'BB' system, 4H).

p-Anisyldimethyl(p-tolyl)tin (4). Colorless liquid. ^{1}H NMR ($CDCl_3$, 80.13 MHz): δ 7.75–7.20 (m, 4H); 7.14 (tolyl BB' system, 2H); 6.90 (anisyl BB' system, 2H); 3.782 (3H); 2.327(3H); 0.459 (s, $^2J(^{119}Sn-^1H)$ 56.7 Hz). MS (16 eV) *m/e* (%) 348 (8); 333 (100); 257 (< 2); 227 (9); 211 (8); 197 (4); 120 (11); 91 (10). Anal. Found: C, 55.77; H, 6.04%. Calc.: C, 55.38; H, 5.81%.

p-Anisylmethylphenyl(p-tolyl)tin (6). Purified by radial TLC (eluted with petroleum ether 60–70 °C: diethyl ether, 95.5:0.5), very low M.P. ^{1}H NMR ($CDCl_3$, 80.13 MHz): δ 7.79–7.26 (m, 9H); 7.16 (tolyl BB' system, 2H); 6.92 (anisyl BB' system, 2H); 3.95 (s, 3H); 2.342 (s, 3H); 0.662 (s, $^2J(^{119}Sn-^1H)$ 56.7 Hz, 3H). (CD_3COCD_3, 200.13 MHz): δ 7.70–7.27 (m, 9H); 7.222 (tolyl BB' system, 2H); 6.990 (anisyl BB' system, 2 H, $^0J \approx 8.4$ Hz); 3.796 (s, 3H); 2.324 (s, 3H); 0.695 (s, $^2J(^{119}Sn-^1H)$ 56 Hz, 3H). ^{13}C NMR (CD_3COCD_3): δ ($J(^{119}Sn-^{13}C)$) −10.87; 21.38 (Ar–CH_3); 55.24 (OCH_3); 115.21 (54.8, C-3 An); 129.23 (49.8, C-3 Ph); 129.56 (10.9, C-4 Ph); 129.89; 130.04 (51.92, C-3 To); 136.16; 137.33 (39.3, C-2 To); 137.36 (37.7, C-2 Ph); 138.52 (43.6, C-2 An); 139.28; 140.44 (C-1 Ph); 161.45 (C-4 An). MS (16 eV) *m/e* (%) 410 (6); 395 (100); 333 (5); 319 (3); 303 (5); 227 (7); 211 (7); 197 (9); 120 (8); 91 (7); 77 (2). Anal. Found: C, 62.1; H, 5.6. Calc.: C, 61.65; H, 5.42%.

Dimethylphenyl(p-tolyl)tin (7). Colorless liquid, purified either by radial TLC or distillation at 142 °C (0.4 mmHg) using a Kugelrohr apparatus. ^{1}H NMR (CD_3COCD_3, 200.13 MHz): δ 7.67–7.25 (m, 7H), 7.187 (tolyl BB' system, $^0J \approx 7.4$; 2H), 2.308 (s, 3H), 0.491 (s, $^2J(^{119}Sn-^1H)$ 56.32 Hz). ^{13}C NMR (CD_3COCD_3): δ ($J(^{119}Sn-^{13}C)$) −10.40; 21.36 (Ar–CH_3); 129.02 (48.2, C-3 Ph); 129.24 (10.9, C-4 Ph); 129.83 (50.2, C-3 To); 136.88 (38.8, C-2 To); 136.91 (37.1, C-2 Ph); 141.60. Anal. Found: C, 56.76; H, 5.93. Calc.: C, 56.83; H, 5.72%.

p-Anisyldimethylphenyltin (8). Colorless liquid, purified either by radial TLC or distillation at 160–170 °C (0.5 mmHg) using a Kugelrohr apparatus. ^{1}H NMR (CD_3COCD_3, 200.13 MHz): δ 7.65–7.20 (m, 7H); 6.950 (*p*-anisyl BB' system, $^0J \approx 8.4$ Hz, 2H), 3.780 (s, 3H); 0.479 (s, $^2J(^{119}Sn-^1H)$ 56.2 Hz.). ^{13}C NMR (CD_3COCD_3): δ ($J(^{119}Sn-^{13}C)$) −10.32 ($SnCH_3$); 55.22 (OCH_3); 115.01 (53.0, C-3 An); 129.02 (48.2, C-3 Ph); 129.24 (10.9, C-4 Ph); 131.24; 136.91 (37.4, C-2 Ph); 138.04 (42.8, C-2 An); 141.26; 161.26. Anal. Found: C, 54.47; H, 5.68. Calc.: C, 54.10; H, 5.45%.

p-Anisyl(p-biphenyl)phenyl(p-tolyl)tin (9). Purified by radial TLC (eluted with petroleum ether 60–70 °C: diethyl ether, 99:1), M.P. 105.0–106.5 °C. ^{1}H NMR (CCl_4 with a capillary tube containing CD_3COCD_3; 200.13 MHz): δ 7.62–7.20 (m, 18H); 7.140 (tolyl BB' system, 2H); 6.875 (anisyl BB' system, 2H); 3.781 (s, 3H); 2.366 (s, 3H). ^{13}C NMR ($CDCl_3$, 200.13 MHz): δ

($J(^{119}Sn-^{13}C)$) 21.50 ($ArCH_3$); 55.01 (OCH_3); 114.55 (56.78, C-3 An); 127.14 (Biph); 127.21 (51.35, Biph); 127.39 (Biph); 128.59 (51.78, C-3 Ph); 128.77 (C-4 Ph); 128.99 (C-1 An); 129.50 (53.68, C-3 To); 134.06; 137.15 (39.62, C-2 To); 137.20 (37.98 C-2 Ph); 137.56 (Biph); 138.36 (42.56 C-2 An); 138.97; 141.02 (C-1 Ph); 141.79 (Biph); 160.53 (C-4 An). MS (70 eV) *m/e* (%) 548 (11); 471 (100); 457 (39); 441 (21); 395 (38); 260 (46); 244 (9); 152 (23). HRMS Found: 548.115277. Calc.: 548.116145. Anal. Found: C, 70.07; H, 5.14. Calc.: C, 70.23; H, 5.16%.

p-Anisyl(p-biphenyl)methyl(p-tolyl)tin (**10**). Purified on a small scale by radial TLC (eluted with petroleum ether 60–70 °C: diethyl ether, 99:1). ^1H NMR (CCl_4 with a capillary tube containing CD_3COCD_3; 200.13 MHz): δ 7.55–7.18 (m, 13H); 7.114 (tolyl BB' system, 2H); 6.848 (anisyl BB' system, 2H); 3.786 (s, 3H); 2.362 (s, 3H); 0.677 (s, $^2J(^{119}Sn-^1H)$ 55.7 Hz, 3H).

p-Anisyl(p-biphenyl)methylphenyltin (**11**). Isolated as a mixture with **10** by radial TLC (eluted with petroleum ether 60–70 °C: diethyl ether, 99:1). ^1H NMR (CCl_4 with a capillary tube containing CD_3COCD_3; 200.13 MHz): δ 0.694 (s, 3H); the other peaks overlap with those of compound **10** (Compound **11** was identified by difference of the spectra).

p-Biphenylmethylphenyl(p-tolyl)tin (**12**). Purified by radial TLC (eluted with petroleum ether 60–70 °C:diethyl ether (99:1), colorless liquid. ^1H NMR (CCl_4 with a capillary tube containing CD_3COCD_3; 200.13 MHz): δ 7.55–7.18 (m, 16H); 7.116 (tolyl BB' system, 2H); 2.355 (s, 3H); 0.699 (s, $^2J(^{119}Sn-^1H)$ 44.6 Hz, 3H).

Methyltriphenyltin (**13**). Synthesized by reaction between $NaSnPh_3$ and methyl iodide in liquid ammonia (90% isolated yield). Purified by radial TLC (eluted with hexane), M.P. 62.5–63.5 °C (lit. [19]: 60–61 °C). ^1H NMR ($CDCl_3$, 60 MHz): δ 8.05–7.08 (m, 15H), 0.67 (s, $^2J(^{119}Sn-^1H)$ 54.5 Hz, 3H); (CCl_4 with a capillary tube containing CD_3COCD_3; 200.13 MHz): δ 7.6–7.0 (m, 15H), 0.699 (s, $^2J(^{119}Sn-^1H)$ 55.72 Hz). MS (25 eV) *m/e* (%) 351 (100), 289 (18), 274 (3), 212 (< 1), 197 (41), 154 (2).

Benzyltriphenyltin (**14**). Purified by radial TLC (eluted with petroleum ether 30–60 °C, M.P. 87.5–89.0 °C (Ref. [20]: 90–91 °C). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.56–6.97 (m, 20H); 2.987(s, $^2J(^{119}Sn-^1H)$ 68.03 Hz; 2H); (CCl_4): δ 2.910 (2H).

Benzyldiphenylmethyltin (**15**). Purified by radial TLC (eluted with petroleum ether 30–60 °C), colorless liquid [21]. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.61–6.99 (m, 15H); 2.768 (s, $^2J(^{119}Sn-^1H)$ 66.59 Hz, 2H); 0.414 (s, $^2J(^{119}Sn-^1H)$ 54.48 Hz, 3H); (CCl_4 with a capillary tube containing CD_3COCD_3; 200.13 MHz): δ 2.689 (2H); 0.364 (3H).

Benzylphenyldimethyltin (**16**). Purified by radial TLC (eluted with petroleum ether 30–60 °C), colorless liquid [21]. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.56–6.96 (m, 10H); 2.528 (s, $^2J(^{119}Sn-^1H)$ 64.87 Hz, 2H); 0.252 (s, $^2J(^{119}Sn-^1H)$ 53.80 Hz, 6H); (CCl_4 with a capillary tube containing CD_3COCD_3; 200.13 MHz): δ 2.462 (2H); 0.216 (6H).

Butyltriphenyltin (**18**). Synthesized by reaction between $NaSnPh_3$ and *n*-butylbromide in liquid ammonia (87% isolated yield). Purified by radial TLC (eluted with petroleum ether 30–60 °C, M.P. 58.5–60.0 °C (lit. [22]: 61–62 °C). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.68–7.34 (m, 15H); 1.80–1.27 (m, 6H); 0.878 (t, 3H). ^{13}C NMR (CD_3Cl_3, 200.13 MHz): δ ($J(^{119}Sn-^{13}C)$ 10.83 (398.2, C-1 Bu); 13.56; 27.29 (65.3, C-2 ó C-3 Bu); 28.76 (22.2 C-2 ó C-3 Bu); 128.41 (48.2, C-3 Ph); 128.75 (11.0, C-4 Ph); 137.03 (35.6, C-2 Ph); 139.14 (480.3, C-1 Ph).

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