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Synthesis of Functionalized Diaryldimethylstannanes from the Me_2Sn^{2-} Dianion by $S_{RN}1$ Reactions

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$$Me_2SnX_2 + Na \xrightarrow{NH_3} Me_2Sn^{2-} \xrightarrow[ArCl]{h\nu} Me_2SnAr_2$$

$$Me_2SnAr_2 \xrightarrow{Cu(NO_3)_2} Ar\text{-}Ar$$

The reaction of different ArCl with the Me_2Sn^{2-} dianion in liquid ammonia under irradiation afforded Ar_2SnMe_2 in good yields (68−85%). The results obtained clearly indicate that the reaction proceeded through an $S_{RN}1$ reaction. As a synthetic application of these Ar_2SnMe_2, the homocoupling is described in the presence of $Cu(NO_3)_2{\cdot}2.5H_2O$ to afford the biaryls. These reactions proceeded almost quantitatively.

The radical nucleophilic substitution or $S_{RN}1$ is a chain process through which an aromatic nucleophilic substitution is obtained. The scope of the process has considerably increased, and nowadays it is an important synthetic possibility to achieve substitution of different substrates.[1] Several nucleophiles can be used such as carbanions and anions from compounds bearing heteroatoms, which react to form new C−C or C−heteroatom bonds in good yields. Many substituents are compatible with the $S_{RN}1$ mechanism.[1] This chain process requires an initiation step. In a few systems, spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed. When the ET does not occur spontaneously, it can be induced by light stimulation.[1] The propagation steps of the $S_{RN}1$ mechanism are presented in Scheme 1. Overall, eqs 1−3 depict a nucleophilic substitution in which radicals and radical anions are intermediates (Scheme 1, eq 1−3).

SCHEME 1

$$
\begin{array}{lr}
(ArX)^{\cdot-} \longrightarrow Ar^{\cdot} + X^{-} & (1) \\
Ar^{\cdot} + Nu^{-} \longrightarrow (ArNu)^{\cdot-} & (2) \\
(ArNu)^{\cdot-} + ArX \longrightarrow ArNu + (ArX)^{\cdot-} & (3) \\
\hline
ArX + Nu^{-} \longrightarrow ArNu + X^{-} & (1\text{-}3)
\end{array}
$$

Most of the nucleophiles studied are monoanions. There are few reports on the reaction of 1,3-dianions from β-dicarbonyl compounds that react quite well through the terminal carbon site under irradiation.[2] Dianions derived from sulfides, such as $^{-}S{-}R{-}S^{-}$ (R = alkyl, aryl), reacted with haloarenes[3] and dihaloarenes.[4,5] Other dianions studied by electrochemical induced reactions were Se_2^{2-} and Te_2^{2-} dianions.[6]

Other types of dianions are those where the negative charges are on only one heteroatom. By reaction with Na metal in liquid ammonia elemental M (M = P, As, Sb) affords an "M^{3-}" species and reacts with PhX (X = I, Cl) under irradiation to form Ph_3M from fair to good yields.[7]

In addition, the dianion prepared in liquid ammonia from elemental Se and Na metal reacts with haloarenes to give $(ArSe)_2$ after oxidation of the $ArSe^{-}$ ions intermediate, or it is trapped with MeI to afford ArSeMe in good yields.[8] Similar results were obtained with Te^{2-} ions.[8]

We have described the photostimulated reactions of Me_3Sn^{-} ions with several ArCl in liquid ammonia that afforded $ArSnMe_3$ from very good to excellent yields (70−100%).[9,10] These stannanes are intermediates in Pd-catalyzed cross-coupling reactions[11,12] and their synthesis extends the scope and applications of the $S_{RN}1$ mechanism.

We hereby report the formation of the dianion Me_2Sn^{2-} in liquid ammonia by the reaction of Me_2SnX_2 (X = Cl or Br) and Na metal, and the novel use of this dianion in a photostimulated reaction with ArCl to obtain Ar_2SnMe_2. As a synthetic application of the stannanes thus obtained, the homocoupling of the Ar_2SnMe_2 mediated by Cu reagents was carried out.

Biaryls are an important type of compound because of their numerous applications.[13] A variety of methods are available for the aryl−aryl C−C bond formation.[14,15] The

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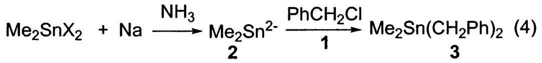
Ullmann coupling has been used for these purposes.[16] Also, many improved methods of this reaction have been developed.[14,17] Moreover, aryl boronic acid,[18] aryl zinc,[17,19] as well as $ArSnR_3$[20–25] are frequently used in the homocoupling of aryls. Several methods based on Cu-mediated or Cu-catalyzed coupling of stannanes have been reported.[20b,21,22] Iyoda et al.[23] described the couplings of Ar_2SnMe_2 with Cu where the Ar_2SnMe_2 were prepared by the reaction of aryllithiums with Me_2SnCl_2. Furthermore, the oxidative homocoupling of $ArSnR_3$ is a useful synthetic method to obtain symmetrical biaryls.[24] Recently, the Cu- and Mn-catalyzed homocoupling of $ArSnR_3$ in the presence of iodine has been achieved.[25]

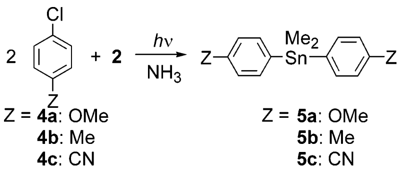
Herein we report the homocoupling mediated by $Cu(NO_3)_2$ of the Ar_2SnMe_2 obtained from the dianion Me_2Sn^{2-} via the $S_{RN}1$ reaction. The synthesis of Ar_2SnMe_2 was carried out in one step, which in most cases requires two steps or lithium reagents.

When Me_2SnX_2 (X = Br or Cl) was treated with Na metal in liquid ammonia, and the reaction was quenched with benzyl chloride (**1**) to trap the dianion **2** formed, the double substitution product $Me_2Sn(CH_2Ph)_2$ (**3**) was obtained in 93% yield (eq 4). It is important to notice that 6 equiv of Na metal are needed to form **2**. When only 4 equiv of the metal were used, only 53% of the isolated product **3** was obtained (Table 1, entries 1 and 2).



$$Me_2SnX_2 + Na \xrightarrow{NH_3} \underset{\mathbf{2}}{Me_2Sn^{2-}} \xrightarrow[\mathbf{1}]{PhCH_2Cl} \underset{\mathbf{3}}{Me_2Sn(CH_2Ph)_2} \quad (4)$$

TABLE 1. Reaction of the Dianion Me_2Sn^{2-} (2) with ArCl in Liquid Ammonia[a]



	substrate (mmol)	Me_2Sn^{2-} (mmol)	conditions (vol)	products	yield[b] (%)
1	**1** (1.6)	0.40	4 equiv Na (400 mL)	**3**	– (53)
2	**1** (1.6)	0.40	6 equiv Na (400 mL)	**3**	93 (86)
3	**4a** (0.4)	0.22	3 h, dark (200 mL)	**5a**	*c*
4	**4a** (0.8)	0.44	3 h, *hν* (400 mL)	**5a** PhOMe	85 (63) 13
5	i.**4a** (19.6) ii.**4a** (22.8)	19.7[d]	i. 1 h, *hν* (700 mL)[e] ii. 1 h, *hν*	**5a**	– (59)
6	**4b** (0.52)	0.20	1 h, dark (200 mL)	**5b**	*c*
7	**4b** (0.52)	0.20	1 h, *hν* (200 mL)	**5b**	81 (63)
8	**4c** (156)	0.60	3 h, dark (400 mL)	**5c** PhCN	68 (63)[f] 10
9	**4c** (0.40)	0.20	3 h, dark, 10% DTBN (250 mL)	**5c**	*c*
10	**4c** (1.0)	0.55	3 h, *hν* (400 mL)	**5c** PhCN	56 (40) 28
11	**6** (0.48)	0.30	3 h, dark (200 mL)	**7**	*c*
12	**6** (1.00)	0.55	3 h, *hν* (400 mL)	**7** Naph	68 (51) 27
13	**8** (0.52)	0.20	2 h, dark (200 mL)	**10**	– (96)
14	**8** (1.04)	0.40	2 h, *hν* (400 mL)	**9**	95

[a] The dianion Me_2Sn^{2-} (**2**) was obtained from Me_2SnX_2 and 6 equiv of Na metal in dry liquid ammonia under nitrogen. [b] By GC with the internal standard method. Isolated yields in parentheses. [c] Substrate was recovered in almost 100% yield. [d] The nucleophile was the Me_3Sn^- ions. [e] After the irradiation, 42 mmol of Na metal was added. [f] Substrate **4c** was recovered in 20% yield.

A dimeric species $(Me_2Sn)_2^{2-}$ may be formed as previously proposed.[26] Evidence of the presence of the dimmer is the formation of the product $(Me_2ArSn)_2$ in the $S_{RN}1$ reactions carried out with the dianion obtained with 4 equiv of Na. When 6 equiv of Na metal was used, this product was not practically observed. Even so the net reaction requires 4 equiv of Na; the extra 2 equiv consumed may be due to the loss of Na by reduction of ammonia.

To evaluate the reactivity of **2** we allowed it to react with ArCl in liquid ammonia under photostimulation. There is no reaction of *p*-chloroanisole (**4a**) with **2** in dark conditions; however, under irradiation it gave the double substitution product **5a** in good yields (Table 1, entries 3 and 4).[27]

On the other hand, we have reported[28] the synthesis of Ar_2SnMe_2 through a two step-one pot procedure in liquid ammonia. Substrate **4a** was added to a solution of Me_3Sn^- ions prepared from Me_3SnCl and Na metal, and then irradiated for 1 h. Next, Na metal was added to obtain the nucleophile $(p\text{-}MeOC_6H_4)Me_2Sn^-$ ions. Substrate **4a** was added again and irradiated for 1 h. The double substitution product **5a** was obtained in 59% isolated yield (entry 5). The result obtained after the two subsequent $S_{RN}1$ reactions was similar to that obtained with the dianion in one reaction (63%), but the later reaction required less time and less experimental work.

Also, there was no reaction of *p*-chlorotoluene (**4b**) in the dark; however, under irradiation, the disubstitution product **5b** was obtained in high yields (entries 6 and 7).

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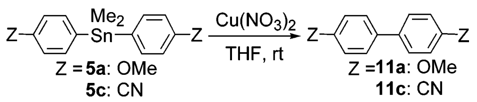
TABLE 2. Homocoupling Reactions of Ar_2SnMe_2 Mediated by $Cu(NO_3)_2$ in THF[a]



entry	substrate	time (h)	products	yield (%)[b]
1	**5a**	2	**11a**	67
2	**5a**	12	**11a**	71
3	**5a**	24	**11a**	99
4	**5c**	24	**11c**	70
5[c]	**5c**	24	**11c**	86
6	$Me_2SnPh(p\text{-}C_6H_4OMe)$ (**12**)	24	*p*-$MeOC_6H_4$−Ph (*p*-$MeOC_6H_4)_2$ $(Ph)_2$	57 17 20
7	**3**	24	PhCHO $PhCH_2OH$	45 42

[a] The reaction was carried out with 1 mmol of the stannane and 2.8 mmol of $Cu(NO_3)_2{\cdot}2.5H_2O$ in 1 mL of THF at room temperature. [b] Determined by GC. [c] The reaction was carried out with 3.6 mmol of $Cu(NO_3)_2{\cdot}2.5H_2O$.

These reactions were carried out with an excess of substrate with respect to the nucleophile. The results obtained in this condition were practically the same as those in the cases where an excess of nucleophile was used.

When *p*-chlorobenzonitrile (**4c**) and **2** were allowed to react in the dark during 3 h, the substitution product **5c** was obtained in 63% yield (entry 8). This reaction was completely inhibited by di-*tert*-butyl nitroxide (DTBN), a well-known inhibitor of $S_{RN}1$ reactions (entry 9).[1] The fact that there is reaction in dark condition, but it is inhibited by DTBN, is indicative that there is a spontaneous ET from **2** to **4c** to initiate the $S_{RN}1$ reaction. The yield of **5c** decreases under irradiation (40%) (entry 10). No increase in the product yield was observed when the reaction was carried out with an excess of the substrate.

There was no reaction of 1-chloronaphthalene (**6**) with **2** in the dark. However, good yields of the disubstitution product di(1-naphthyl)dimethylstannane (**7**) were obtained under irradiation (entries 11 and 12). When the potassium salt of 3-chlorobenzoic acid (**8**) was allowed to react with **2** in dark conditions there was no reaction and the 3-chlorobenzoic acid (**10**) was obtained in 96% yield (entry 13). The photostimulated reaction with the potassium salt **8** gave only the reduction product benzoic acid (**9**) (entry 14).

On the other hand, as a synthetic application of the Ar_2SnMe_2 obtained, the homocoupling reaction of Ar_2SnMe_2 mediated by $Cu(NO_3)_2$ was carried out in THF. These reaction conditions are similar to the ones described by Iyoda et al.;[23] however, we used $Cu(NO_3)_2{\cdot}2.5H_2O$ and the reaction required longer time. The coupling reactions are summarized in Table 2.

The homocoupling reaction of **5a** mediated by $Cu(NO_3)_2$ gave 4,4′-dimethoxybiphenyl (**11a**) in excellent yields (entries 1−3). With longer reaction time, the coupling product yields were higher. The reaction needed 24 h to be completed (entry 3). Also, with an electron withdrawing substituent on the aromatic ring such as CN, **5c**, the homocoupling reaction took place (entry 4). To obtain higher yields of the biaryl **11c** (86%), more $Cu(NO_3)_2$ was needed (entry 5).

The coupling of an asymmetrical stannane was studied to know the scope of the homocoupling reactions. The coupling of the asymmetrical phenyl(*p*-methoxyphenyl)-dimethylstannane **12** in the same reaction conditions described above led to three different products, one from the cross coupling of the two aryls affording the asymmetrical biaryl (57%) and two others corresponding to the coupling of the same aryls themselves affording the symmetrical biaryls (entry 6). No coupling products were found in the reaction carried out with the benzylic stannane **3** (entry 7). We only observed the oxidation products.

We also carried out the one-pot reaction from **4a** to the biaryl **11a** without isolation of the stannane. The procedure was found to be possible. In this reaction the overall yield was 42% of the biaryl **11a**.

In conclusion, we developed a new approach to obtain Ar_2SnMe_2 and also an application of the stannanes obtained. Even though the direct oxidative homocoupling of Ar_2SnMe_2 to achieve the symmetrical biaryls was described,[24,25] this approach could be an interesting alternative in view that this method presents the advantage that involves the use of less tin during the whole process.

Experimental Section

General Procedure for the Photostimulated Reaction of Me_2Sn^{2-} Dianion in Liquid Ammonia. The following procedure of the reaction of **4a** with Me_2Sn^{2-} dianions is representative of all the reactions. Into a three-necked, 500-mL, round-bottomed flask equipped with a coldfinger condenser charged with dry ice-ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 400 mL of ammonia previously dried with Na metal under nitrogen. The Me_2SnBr_2 (0.44 mmol) was added and then 6 equiv of Na metal (2.64 mmol) in small pieces, waiting for bleaching between each addition. After 20−30 min of the last addition **4a** (0.80 mmol) was added and then irradiated for 3 h. The reaction was quenched by adding NH_4NO_3 in excess, and the ammonia was allowed to evaporate. The residue was dissolved in water and next extracted with diethyl ether. The product **5a** was quantified by GC, using the internal standard method, yielding 85% of product. The product **5a** was isolated by vacuum distillation by using a Kügelrohr apparatus, yielding 63% of the isolated product. Column chromatography seems to be an unsuitable purification method for these stannanes, since they decompose in long contact with silica gel. The product was characterized by ^1H NMR, ^{13}C NMR, and GC-MS. All these spectroscopic date agreed with those reported in the literature for this compound **5a**,[29] and for the other stannanes obtained, **5b**,[29] **7**,[30] and **3**.[31] ^1H NMR and ^{13}C NMR spectra are provided in the Supporting Information.

Following the general method described above, **5c** was obtained as a white crystalline solid (mp 118−119 °C). ^1H NMR (200 MHz, $CDCl_3$): δ 7.40−7.75 (m, 8H), 0.61 (s, 6H, J_{Sn-H} = 56 Hz). ^{13}C NMR (60 MHz, $CDCl_3$): δ 147.0, 136.5 (J_{Sn-C} = 39 Hz), 131.2 (J_{Sn-C} = 47 Hz), 118.6, 112.6, −2.0. Mass spectra *m/z* (rel intensity): 352 (6) M^+, 339 (100), 252 (14), 222 (45), 120 (26), 103 (4). HRMS for $C_{16}H_{14}N_2Sn$ (M^+) 352.0179, found 352.0182.

One-Pot Synthesis of 5a from Me_3SnCl in Liquid Ammonia (Table 1, entry 5). To 800 mL of dry liquid ammonia treated as before, the Me_3SnCl (19.7 mmol) was added and then Na metal (43.5 mmol) in small pieces, waiting for bleaching

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between each addition, to form Me_3SnNa. Later, **4a** (19.6 mmol) was added to this solution and then irradiated for 1 h. The equipment was taken from the photochemical reactor, and then Na metal (38.4 mmol) was added to form the second nucleophile (*p*-anisyl)dimethylstannylsodium. Then, **4a** (22.8 mmol) was added to this solution, which was then irradiated for 1 h. The reaction was quenched and treated as explained before. The product **5a**[29] was quantified by GC with use of the internal standard method, yielding 59% of product.

Homocoupling Reaction of the Stannanes Mediated by $Cu(NO_3)_2 \cdot 2.5H_2O$. The following procedure is representative of all these reactions. Into a 10 mL reaction tube and a magnetic stirrer, 1 mL of THF was added, and afterward the stannane **5a** (1 mmol). Next, the $Cu(NO_3)_2 \cdot 2.5H_2O$ (2.8 mmol) was added to this solution, which was stirred at room temperature for 24 h. Then, water (20 mL) and Cl_2CH_2 (20 mL) were added and extracted three times with Cl_2CH_2. The product was quantified by GC, using the internal standard method, yielding 99% of **11a**. The biaryl product was isolated by radial thin-layer chromatography with plates of 2 mm (silica gel 60 PF_{254}), using hexanes–Cl_2CH_2 mixtures as eluants. The product was characterized by ^1H NMR, ^{13}C NMR, and GC-MS. The spectroscopic date agreed with those reported in the literature for this compound **11a**,[32] and also for the product **11c**.[33]

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Supporting Information Available: Experimental details and characterization data of the stannane compounds (^1H NMR and ^{13}C NMR spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

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