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Mechanistic studies on the reactions of trimethylsilanide and trimethylstannylide ions with haloarenes in hexamethylphosphoramide

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Abstract

The large positive ρ values obtained from Me_3M^- ions reacting with appropriately-substituted chloroarenes (4.1 ± 0.1, and 2.94 ± 0.02 for M = Sn and Si, respectively) can be accounted for the presence of a strong negative charge in the transition state of the substitution reaction. These ρ values for Me_3Sn^- and Me_3Si^- nucleophilic attack on ArX provide evidence for the overall larger selectivity of the former, compared with the more reactive, and less selective Me_3Si^- ions. When 1-allyloxy-2-halobenzenes (X = Cl, I) are allowed to react with Me_3Sn^- ions in HMPA, an *ipso* substitution product **6** is obtained, in addition to stannylated products on the allylic moiety. This reaction proceeds by a HME process, as opposed to the same reaction carried out in liquid ammonia, where (2,3-dihydro-benzofuran-3-ylmethyl)-trimethylstannane (**4**) is furnished in high yield through an $S_{RN}1$ mechanism. Reaction of Me_3Si^- ions with 1-allyloxy-2-iodobenzene in HMPA, affords only the *ipso*-substituted product, namely 2-(allyloxy-phenyl)-trimethylsilane (**11**), through the intermediacy of a hypervalent silicon species. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Trimethylsilanide ions; Trimethylstannylide ions; $S_{RN}1$ reaction, HME reaction; Hypervalent silicon

1. Introduction

Trimethylstannide ions (Me_3Sn^-) have been shown to react with PhX (Cl, Br, and I) in tetraglyme as solvent to produce the substitution product $PhSnMe_3$, and variable amounts of reduction product benzene. Mechanistic studies in this system revealed that the reaction occurs by a Halogen Metal Exchange (HME) process in a solvent cage [1]. When THF is used as solvent, Me_3Sn^- ions react with *o*-, *m*-, and *p*-bromotoluenes to afford the expected trimethylstannyl-substituted products [2].

On the other hand, when *p*-chloro and *p*-fluorotoluenes are allowed to react with Me_3Sn^- ions in THF as solvent, the yields of *cine* substitution products are enhanced. Radical traps favor *cine* substitution products, and Li metal enhances the yields of *ipso* substitution. From these results it was concluded that the reactions should proceed, at least partially, by a radical mechanism [2].

We have recently described photostimulated reactions of chloroarenes with triorganylstannyl ions by the $S_{RN}1$ mechanism in liquid ammonia. These reactions afford moderate-to-excellent yields of the nucleophilic substitution products. Bromo and iodoarenes react by an HME reaction [3,4]. When the aromatic substrate bears two leaving groups, such as in *p*- and *m*-dichlorobenzenes, disubstitution products are obtained in 88–90% yield [5]. The monosubstitution products are not intermediates in these reactions.

Trimethylsilanide ions (Me_3Si^-) cannot be prepared in liquid ammonia due to reaction of this ion with the solvent, to afford silylamines [6]. We have recently reported the enhanced reactivity of Me_3Si^- ions in HMPA toward PhX (Cl, Br, I) to afford very good yields of $PhSiMe_3$ [7]. On the other hand, PhF reacts with Me_3Si^- ions to afford 76% of *o*- and *p*-trimethyl-

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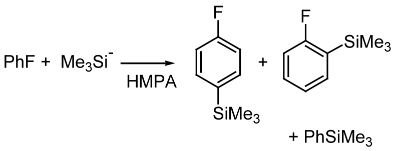
silylfluorobenzenes, and 14% of $PhSiMe_3$ according to Eq. (1).



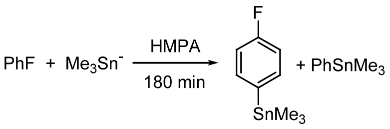
(1)

Pyridine yields a quantitative yield of 4-trimethylsilanylpyridine [7] and *N*-methyl indole affords *N*-methyl-(2-trimethylsilanyl)indole in 78% of isolated yield [8]. Benzene itself reacts in the dark with Me_3Si^- ions to afford 45% yield of $PhSiMe_3$. Experiments aimed at elucidating the mechanism of these reactions where a H atom is substituted by the TMS group were carried out. Both PhF and benzene show pronounced deuterium kinetic isotope effects (3.2 ± 0.1 and 1.7 ± 0.1, respectively) [7].

It has been proposed that the nucleophilic attack of Me_3Si^- ions on aromatic moieties take place through the intermediacy of hypervalent silicon species, which evolve to products through loss of an appropriate leaving group (X in the case of haloarenes, and H in the case of non-activated aromatic hydrocarbons or heteroaromatic compounds without formal leaving groups).

PhX (X = I, Br) react with Me_3Sn^- ions in HMPA through a HME process. ArCl substrates undergo a slow HME reaction with Me_3Sn^- ions. These reactions are slightly accelerated upon photostimulation, indicating that an ET process competes with a polar mechanism. However, when *p*-dichlorobenzene is allowed to react with Me_3Sn^- ions in HMPA, both *p*-chlorotrimethylstannylbenzene and *p*-bis-trimethylstannylbenzene are formed [8], as opposed to when the same reaction is carried out in liquid ammonia, where the monosubstitution product is not an intermediate.

PhF conforms to a special case in the sense that the intervention of a hypervalent tin species is postulated in order to account for products such as *p*-fluorophenyltrimethylstannane. The ET process also operates under irradiation to yield the straightforward substitution product $PhSnMe_3$ together with *p*-fluorophenyltrimethylstannane (Eq. (2)). The fact that only the *p*-isomer is formed, as opposed to the same reaction carried out with Me_3Si^- ions which renders both the *o*- and *p*- TMS-substituted fluorobenzenes, suggests that the Me_3Sn^- ions are less reactive, and more selective than Me_3Si^- ions.



(2)

Considering the mechanistic evidence amounted for the reactivity of Me_3Sn^- ions toward PhX in different solvents and given the enhanced reactivity of Me_3Si^- anion in HMPA toward haloarenes, we embarked on providing further mechanistic evidence for the reactions of the Me_3Si^- and Me_3Sn^- ions toward haloarenes in HMPA.

2. Results and discussion

The reactivity order in competition reactions of Me_3Si^- ions with PhX in HMPA was found to be PhI (3.5):PhBr (1.9):PhCl (1):PhF (0.08) [7]. These results show that the span in reactivity between the four halogens toward Me_3Si^- ions is, from PhF to PhI, only about 44 [7]. It has been suggested that these nucleophilic substitutions take place through a silicon hypervalent intermediate. The span in reactivity in competition experiments of the four halobenzenes toward acetone enolate anion in liquid ammonia in $S_{RN}1$ reactions is over 100 000 [9] and Kuivila et al. found that the relative reactivity of PhX versus Me_3Sn^- ions in tetraglyme was ca. PhI (10^6):PhBr (10^5):PhCl (1) [1]. These reactions proceed by an in-cage HME mechanism. This notorious span in reactivity is expected in pure HME processes.

In contrast, competition experiments, carried out in the dark, among PhX toward Me_3Sn^- ions in HMPA throw a relative reactivity pattern of PhI (77):PhBr

Table 1
Competition experiments of PhX (X = F, Cl, Br, and I) for Me_3Sn^- and Me_3Si^- ions in HMPA

Substrates (mM)	Anion (mM) [a]	Products (relative %) [b]
p-$CH_3C_6H_4Cl$ (4338); PhI (482)	Me_3Sn^- (482)	*p*-$CH_3C_6H_4SnMe_3$ (1.5%); $PhSnMe_3$ (98.7%)
p-$CH_3C_6H_4Cl$ (964); PhBr (482)	Me_3Sn^- (482)	*p*-$CH_3C_6H_4SnMe_3$ (5.1%); $PhSnMe_3$ (95.1%)
p-$CH_3C_6H_4Cl$ (482); PhF (4338)	Me_3Sn^- (482)	*p*-$CH_3C_6H_4SnMe_3$ (88.7%); *p*-$FC_6H_4SnMe_3$ (11.2%) [c]
p-$CH_3C_6H_4Cl$ (85); PhI (85)	Me_3Si^- (49)	*p*-$CH_3C_6H_4SiMe_3$ (22.5%); $PhSiMe_3$ (77.8%) [d]
p-$CH_3C_6H_4Cl$ (85); PhBr (85)	Me_3Si^- (49)	*p*-$CH_3C_6H_4SiMe_3$ (32.1%); $PhSiMe_3$ (67.9%) [d]
p-$CH_3C_6H_4Cl$ (85); PhF (85)	Me_3Si^- (49)	*p*-$CH_3C_6H_4SiMe_3$ (92.6%); $PhSiMe_3$ (7.4%) [d]

[a] Reaction conditions: dark, 25 °C, Me_3Sn^- 3 h, Me_3Si^- (0.25 h).

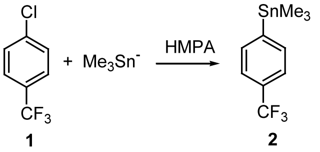
[b] Product yields based on starting PhX, corrected to 1:1 relative molar concentration. The relative yields result from average of duplicate experiments whose $\Delta\varepsilon \leq 2\sigma$.

[c] Upon irradiation (3 h, 366 nm) of a mixture consisting of *p*-$CH_3C_6H_4Cl$ (482 mM), PhF (482 mM), and Me_3Sn^- (482 mM) in HMPA, product relative yields are the following: *p*-$CH_3C_6H_4SnMe_3$ (90.6%), $PhSnMe_3$ (2.9%), *p*-$FC_6H_4SnMe_3$ (6.5%).

[d] The same ratio of relative yields was also obtained, within experimental errors, under the following different reaction conditions: *p*-$CH_3C_6H_4Cl$ (255 mM), PhX (255 mM), and Me_3Si^- (147 mM), reaction time: 1 h.

(19):PhCl (1):PhF (0.13) (Table 1). In this case, the span in reactivity is ca. 590, which when compared with Me_3Si^- ions, denotes a larger selectivity for the reactions of Me_3Sn^- with PhX (being Me_3Si^- ions more reactive, are hence rendered less selective).

p-Chlorobenzotrifluoride **1** reacts with Me_3Sn^- ions in HMPA in the dark to furnish trimethyl-(4-trifluoromethyl-phenyl)stannane (**2**) in 85% yield (Eq. (3)). The *meta* isomer is not observed under our detection limits (< 0.5%) [10].



(3)

Linear free energy relationships (LFER) or Hammett plots were constructed with Me_3Sn^- and Me_3Si^- ions upon reacting in the dark with appropriately-substituted chloroarenes ArCl (*p*-XPhCl, where $X = CH_3O$, CH_3, H, F, Cl, CF_3).

The slopes of these plots (obtained from plotting the log of k_{ArCl}/k_{PhCl} vs. substituent constant σ) yielded ρ values of 4.1 ± 0.1 for the reactions of Me_3Sn^- ions, and $\rho = 2.94 \pm 0.02$ for the reactions of Me_3Si^- ions (Table 2), indicating, in these cases, that a negative charge in the transition states of the substitution reactions of ArX either with Me_3Sn^- or Me_3Si^- ions is strongly developing (Fig. 1).

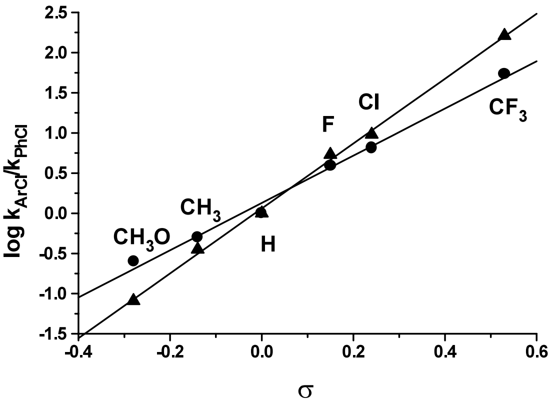
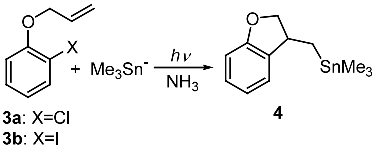


Fig. 1. Hammett plots for the reactions of Me_3Sn^- (▲) and Me_3Si^- (●) ions with ArX in HMPA.

In order to determine the nature of the intermediates involved in the reactions of haloarenes with Me_3Sn^- and Me_3Si^- ions, we examined the behavior of *o*-(2-propenyloxy)halobenzenes (**3**) with these ions as radical probes.

When *o*-(2-propenyloxy)chlorobenzene (**3a**) is subjected to reaction with Me_3Sn^- ions in liquid ammonia, (2,3-dihydro-benzofuran-3-yl-methyl)-trimethyl-stannane (**4**) is obtained (87%) exclusively (Eq. (4)) (Table 3, experiment 1).



(4)

This result is explained by the intermediacy of the $S_{RN}1$ mechanism [11]. When **3a** accepts one electron, radical anion $\mathbf{3a}^{-\bullet}$ is formed, which fragments into radical **5**. This radical intermediate is trapped by the

Table 2
Competition experiments of PhCl and *p*-RC_6H_4Cl toward Me_3M^- ions (M = Sn, Si) [a]

Experiment	*p*-RC_6H_4Cl	Me_3M^-	Relative yields (%)		log k_{ArCl}/k_{PhCl}
	R	M	$PhMMe_3$	*p*-$RC_6H_4MMe_3$	
1	MeO	Sn	92.5	7.5	−1.09
2	Me	Sn	74.0	26.0	−0.45
3	F	Sn	9.8	90.2	0.96
4	Cl	Sn	9.5	90.5	0.98
5	CF_3	Sn	0.60	99.4	2.21
6	OMe	Si	79.9	20.1	−0.60
7	Me	Si	66.6	33.4	−0.30
8	F	Si	20.4	79.6	0.59
9	Cl	Si	13.4	86.6	0.81
10	CF_3	Si	2.1	97.9	1.67

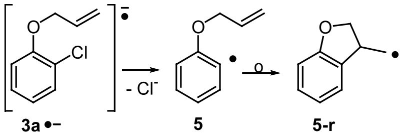
[a] In the reactions with Me_3Sn^- ions, the concentration of the nucleophile, PhCl and *p*-RC_6H_4Cl were 360 mM each in HMPA. The reactions were allowed to proceed for 2 h at 40 °C. For the reactions with Me_3Si^- ions, the concentration of the nucleophile was 490 mM, and PhCl and *p*-RC_6H_4Cl were 980 mM in HMPA respectively. The reactions were allowed to proceed for 2 h at 40 °C. Yields were calculated based on the internal standard method, using trimethylsilylbenzene or trimethylstannylbenzene as calibrated internal standards. Values of k_{ArCl} were calculated based on disappearance of starting materials (PhCl, and ArCl), employing the following expression: $k_{PhCl}/k_{ArCl} = \ln[(PhCl)_o/(PhCl)_t]/\ln[(ArCl)_o/(ArCl)_t]$, where $(PhCl)_o$ and $(ArCl)_o$ are the initial concentrations and $(PhCl)_t$ and $(ArCl)_t$ are the concentrations at time *t*. See: J.F. Bunnett, in: E.S. Lewis (Ed.), Investigation of rates and mechanism of reactions, third ed., Part I, Wiley-Interscience, NY, 1974. The relative yields were the result of an average of duplicate experiments with standard deviation less than 2σ.

Table 3
Reactions of *o*-(2-Propenyloxy)halobenzenes (**3**) with $SnMe_3^-$ ions in HMPA [a]

Experiment	Substrate (mM)	$SnMe_3^-$ (mM)	Reaction conditions	Product(s) (%) [b]
1 [c]	**3a**, (10)	10	hν, 90 min	**4** (87) [d]
2	**3a**, (313)	418	Dark, 120 min	**6** (6), **7** (23), **8** (ca. 4%) [e]
3	**3a**, (313)	418	hν, 90 min	**6** (16), **7** (29), **8** (10) [f]
4	**3b**, (415)	418	Dark, 120 min	**6** (38), **7** (35), **7-r** (12), **8a** (13)
5	**3b**, (751)	1352 [g]	Dark, 120 min	**11** (51) [h]
6	**3b**, (128)	256 [g]	Dark, 24 h	**11** (75), **7** (5) [i]

[a] HMPA (2–7 ml) under N_2.
[b] Determined by glc, unless otherwise indicated.
[c] In 200 ml of liquid ammonia.
[d] Isolated yield.
[e] Substrate recovered in 69% yield.
[f] Substrate recovered in 39% yield.
[g] The nucleophile was Me_3Si^- ions.
[h] Substrate recovered in 49% yield.
[i] Substrate recovered in 24% yield.

double bond faster than coupling with the nucleophile occurs, affording the rearranged radical **5-r** (Eq. (5)). Radical **5-r** reacts with Me_3Sn^- ions to yield **4** (Eq. (6)). There is precedent that rearrangement of radicals can occur along the $S_{RN}1$ mechanism [12].



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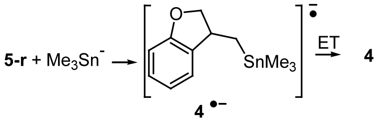
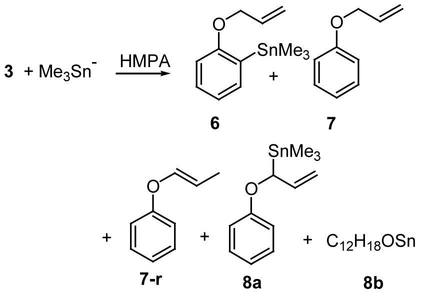


(6)

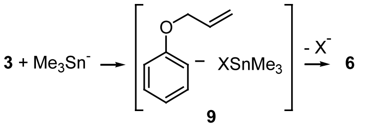
On the contrary, when **3a** is treated with Me_3Sn^- ions in HMPA, (2-allyloxy-phenyl)-trimethyl-stannane (**6**) is found in low yield in the reaction mixture (6%), along with allyloxy-benzene (**7**) (23%), and traces of a rearranged reduction product **7-r** (Eq. (7)). Other substitution products resulting from stannylation on the allyl moiety (**8**, ca. 4% yield) are observed. This reaction is slightly accelerated by light (Table 3, experiments 2–3).



(7)

On the other hand, when **3b** is treated in the dark with Me_3Sn^- ions, 38% of **6** is obtained. The yield of **6** is not enhanced upon photostimulation of the reaction mixture. Reduction products **7** and **7-r** are found in 34 and 12% yields, respectively. This is supporting evidence for the absence of free radicals in the HMPA solution. Product **8a** (13%, vide infra) was not isolated from the reaction mixture but identified by a GC-spike experiment with an authentic sample synthesized by an independent route (see Experimental). The low combined yields of products **8** precluded their direct isolation from the reaction mixture. Product **8b** was tentatively identified on the basis of its GCHRMS data as being probably another positional isomer of **8a** (presumably trimethyl-(3-phenoxy-allyl)-stannane)).

The reduction products observed (i.e. **7** and **7-r**) do not arise by proton abstraction from the solvent; (cf. reaction of PhI with Me_3Sn^- which yields 98% of substitution product, where reduction product benzene is not observed [8]). It is proposed, instead, that when **3** reacts with Me_3Sn^- ions by a HME reaction, ion pair **9** is formed, which collapses to product **6** (Eq. (8)). A H^+ shift from the allyl group to the ring, renders anion **10-r**, which is trapped by Me_3SnX to yield **8**, or it is protonated when the reaction is quenched to afford **7** (Eq. (9)).



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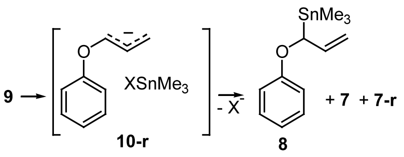
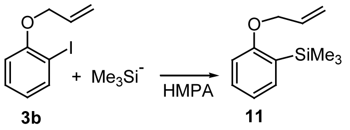


(9)

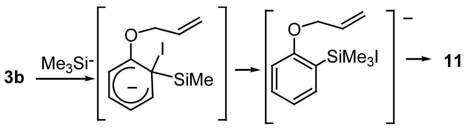
It is noteworthy that though the reaction of **3a** with Me_3Sn^- ions is accelerated by light, no cyclized product is obtained, which is probably indicating that an in-cage ET process is taking place to some extent in the substitution reaction by Me_3Sn^- ions.

In the same fashion, when **3b** is treated with Me_3Si^- ions in HMPA, (2-allyloxy-phenyl)-trimethylsilane (**11**) is obtained according to Eq. (10).



(10)

The reaction pathway for the formation of **11** is not likely to be through silicon-analog intermediates such as **9** or **10-r**, as no reduction products are observed in this case (either **7** or **7-r**) from the reaction mixture. Instead, the exclusive formation of **11** suggests that the intermediate in this reaction is a silicon hypervalent species (Eq. (11)), as it has been proposed for the reactions of PhX with Me_3Si^- ions [7]. At longer reaction times (24 h) the yield of **11** increases up to 75%, and a small amount of **7** (5%) is found.



(11)

3. Conclusions

The large positive ρ values obtained from Me_3M^- ions reacting with PhX (4.1 ± 0.1, and 2.94 ± 0.02 for M = Sn and Si, respectively) can be accounted for the presence of a strong negative charge in the transition state of the substitution reaction. As far as we are concerned, the influence of substituents on nucleophilic substitution rates of ArX substrates by stannyl or silyl anions has not been reported. ρ Values for Me_3Sn^- and Me_3Si^- nucleophilic attack on ArX substrates provide evidence for the overall larger selectivity of the former, compared with the more reactive, and less selective Me_3Si^- ions.

When 1-allyloxy-2-halobenzenes (X = Cl, I) are allowed to react with Me_3Sn^- ions in HMPA, an *ipso* substitution product **6**, in addition to stannylated products on the allylic moiety, are obtained, indicating that the reaction occurs by an HME process, as opposed to the same reaction carried out in liquid ammonia, where the ring closure product (2,3-dihydro-benzofuran-3-ylmethyl)-trimethylstannane (**4**) is furnished in high yield through an $S_{RN}1$ mechanism. On the contrary, 1-allyloxy-2-iodobenzene reacts with Me_3Si^- ions to afford only the straightforward substitution product, through a hypervalent silicon intermediate, ruling out an ET and HME processes. It is interesting to note that 1-allyloxy-2-halobenzenes react by three different mechanisms (i.e. HME, ET, and through hypervalent metallic species), depending on the solvent and on the nucleophile.

4. Experimental

4.1. General methods

Gas chromatographic analyses were performed on a Hewlett–Packard 5890 Series II instrument with a flame ionization detector, a Hewlett–Packard 3396 Series III integrator, an one of the following columns: HP1 5 m × 0.17 mm column, and a DB-1, 30 m × 0.17 mm column. ^{1}H-NMR (200.13 MHz) and ^{13}C-NMR (50.32 MHz) were conducted on a Bruker AC 200 spectrometer in deuterochloroform as solvent or other solvent as indicated. Coupling constants (J) are given in Hz units. GCMS analyses were carried out on a Shimadzu GCMS QP 5050 spectrometer equipped with a DB-5, 30 m × 0.18 mm ID column. IR spectra were conducted on a JASCO instrument, and referenced to polystyrene. The absorptions are given in wavenumbers (cm^{-1}). High resolution mass spectra were conducted at the McMaster Regional Center for Mass Spectrometry, at McMaster University, Canada.

4.2. Materials

PhX (I, Br, Cl, F), *p*-chlorotoluene, *p*-dichlorobenzene, *p*-chloroanisole, *p*-chlorobenzotrifluoride, *p*-chlorofluorobenzene, trimethylsilylbenzene, trimethyltinchloride, *p*-bis-trimethylsilylbenzene, hexamethyldisilane, sodium methoxide, *p*-dinitrobenzene, di-*tert*-butylnitroxide, *N*-chlorosuccinimide, phenol, allyl bromide, potassium carbonate, dimethylformamide, hexane, decane, and eicosane were commercially available and used as received from the supplier. HMPA was distilled twice under reduced pressure and kept under nitrogen.

4.3. Reactions of ArX with Me_3Sn^- ions in HMPA

Into a 15 ml tube previously flame-dried, Na metal (1.8 mmol) and HMPA (2.5 ml) were introduced and the tube sealed with a rubber septum. The suspension was stirred with a micro stir bar and was de-oxygenated and blanketed with a nitrogen atmosphere thrice, and left under N_2. The stirred suspension turned slowly deep blue, and a deoxygenated solution of Me_3SnCl (ca. 0.93 mmol) in HMPA (1 ml) was slowly introduced by syringe and the solution left stirring for additional 20 min. The mixture turned colorless, with some Na suspended. The tube was immersed in an ultrasound bath, and left under sonication until all Na was dissolved and reacted with Me_3SnCl (from 2 to 3 h). At this point, the solution was deep orange. The deep orange solution obtained was indicative of the formation of Me_3Sn^- ions. At this time, for the dark arm of reactions, the tube was covered with aluminum foil to protect it from laboratory light, removed from the ultrasound bath, and the neat ArX (ca. 0.84 mmol) was slowly introduced by syringe through the rubber septum. The dark reactions were left to progress under stirring, whereas the photochemical counterparts were irradiated in a photochemical reactor employing two medium pressure (400 W) water-cooled Hg lamps emitting maximally at 366 nm. The mixtures were then cooled down in an ice bath and quenched slowly with water and extracted three times into pentane. The pentane layers were washed twice with doubly-distilled water. The organic layers were gathered and dried over sodium sulfate, filtered, evaporated and chromatographed (for isolation purposes, the number of moles of the reactants was scaled up by a factor of 10, and the solvent volume, HMPA, was 7.5 ml) over a 2 mm thickness silica-gel plate using radial chromatography (solvent of elution was hexane). The isolated compounds were characterized by standard spectroscopic techniques ($^1H/^{13}C$-NMR, and MS). For GC quantification, the internal standard method was used, employing trimethylsilylbenzene, trimethylstannylbenzene, eicosane or *n*-decane as internal standards.

The standardized procedure for the reactions of trimethylsiliconide ions is given in reference [7].

Phenyltrimethyltin and trimethylphenylsilane were isolated and their spectroscopic data compared with those of authentic samples. Trimethyl-*p*-tolyl-stannane [13], (4-chlorophenyl)-trimethylstannane [14], (4-fluorophenyl)-trimethylstannane [13,15], 1,4-bis-trimethylstannanyl-benzene (**6**) [13], (4-methoxy-phenyl)-trimethylstannane [13], trimethyl-(4-trifluoromethyl-phenyl)-stannane [13], were characterized by standard spectroscopic techniques and the data matched well with those reported in the literature. Analogously, trimethyl-*p*-tolyl-silane [13,16,17], (4-methoxy-phenyl)-trimethylsilane [13,17], (4-chlorophenyl)-trimethylsilane [17,18], (4-fluorophenyl)-trimethyl-silane [13,16,17], trimethyl-(4-trifluoromethyl-phenyl)-silane [13,17], trimethyl-(3-trifluoro-phenyl)-silane [16,17], 1,4-bis-trimethylsilanyl-benzene, 1-allyoxy-2-chloro-benzene (**3a**) [19], 1-allyoxy-2-iodo-benzene (**3b**) [19], were characterized by standard techniques, and the spectroscopic data matched well with those reported in the literature. Allyloxy-benzene and 1-propenyloxy-benzene were characterized by ^1H-NMR and GC–MS data and compared with literature values [19].

4.4. Synthesis and characterization of substrates

4.4.1. (1-Chloro-allyloxy)-benzene

This compound was synthesized from allyloxybenzene and *N*-chlorosuccinimide, according to the following procedure: Into a 50 ml two-necked round-bottomed flask equipped with a water-cooled condenser, and an inlet for a thermometer, allyloxybenzene (11.2 mmol), *N*-chlorosuccinimide (22.4 mmol), benzoyl peroxide (0.95 mmol) and previously distilled CCl_4 (25 ml) were introduced. The reaction flask was heated in an oil bath at 60 °C for 48 h. The reaction mixture was filtered, then quenched with water, and extracted into CCl_4. The organic layers were dried over sodium sulfate, filtered, evaporated. The reaction mixture contained two major products chlorinated at position 1 and another at position 3 of the allyl chain, that is, (3-chloropropenyloxy)-benzene, and (1-chloro-allyloxy)-benzene. The mixture was chromatographed over silica-gel using column chromatography. The elution solvent was petroleum ether. Standard spectroscopic techniques were used to characterize these compounds.

4.5. Syntheses of tin-derived products

4.5.1. (2,3-Dihydro-benzofuran-3-ylmethyl)-trimethylstannane (**4**)

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. Trimethyltin chloride (1.15 mmol) was then added and Na metal (2.65 mmol) in small pieces was introduced, waiting for total de-coloration between each addition. A lemon–yellow solution is obtained. Substrate **3a** (1 mmol) was dissolved in 1 ml of anhydrous ethyl ether and added to the solution. The reaction mixture was irradiated for 120 min (366 nm), and then quenched by adding ammonium nitrate in excess. The ammonia was allowed to evaporate and water (50 ml) was then added. The aqueous phase was extracted with CH_2Cl_2 (3×50 ml) and the organic layers were dried over anhydrous $MgSO_4$. The solvent was evaporated and product **4** was purified by silica-gel column chromatography (isolated product yield: 87%) using a mixture of CH_2Cl_2: petroleum ether (60–80 °C), 15:85. Product **4** was characterized by ^1H-NMR and ^{13}C-NMR, IR, EIHRMS, and GC–MS data as follows.

^1H-NMR ($CDCl_3$) δ (ppm): 0.06 (ss, 9H), 1.32 (double quintet, 2H); 3.76 (octet, 1H, $J = 8.4$, 13.2 Hz); 4.04 (dd, 1H, $J = 8.4$, 7.3 Hz); 4.65 (dd, 1H, $J = 8.4$, 8.76 Hz), 6.83 (cplx m, 2 H); 7.12 (cplx.m, 2 H). ^{13}C-NMR ($CDCl_3$) δ (ppm): −9.49, 17.19, 40.43, 79.16, 109.59, 120.53, 123.84, 125.54, 133.47, 159.56. GC–MS (*m*/*z*, %): 298 ($[M]^+$, 2), 283 (isotopic cluster, 91), 281 (64), 279 (39), 253 (5), 249 (2), 225 (4), 223 (2), 221 (2), 185 (21), 165 (67), 163 (42), 161 (33), 151 (23), 133 (100), 131 (58), 115 (11), 105 (32), 91 (24), 77 (43), 65 (12), 51 (8). EIHRMS: ($[M]^+ - 15$ for $C_{11}H_{15}O^{120}Sn$): 283.0145. Calc.: 283.0145. IR (NaCl pellet) ν (cm^{-1}): 2974, 2896 (s), 1610 (m), 1597 (s), 1481 (s), 1460 (s), 1224 (s), 970 (m), 748 (s), 526 (s).

4.5.2. *(2-Allyloxy-phenyl)-trimethylstannane (**6**)*

This compound [20] was isolated (38% yield) as indicated above from reaction of 1-allyloxy-2-iodobenzene and Me_3Sn^- ions in HMPA, according to the general procedure (vide supra), and characterized by ^{1}H-NMR and ^{13}C-NMR, EIHRMS, and GC–MS data as follow: ^{1}H-NMR (in CD_3CN) δ (ppm): 0.25 (ss, 9H), 4.54 (dt, 2H, $J = 1.82$, 3.3, 8.4 Hz), 5.26 (dq, 1H, $J = 1.82$, 3.3, 10.6 Hz), 5.39 (dq, 1H, $J = 1.82$, 3.6, 17.5 Hz), 6.09 (double quintet, 1 H, $J = 5.12$, 10.6, 15.7 Hz), 6.93 (cplx.m, 2H), 7.35 (cplx.m, 2H). ^{13}C-NMR (in CD_3CN) δ (ppm): −8.74, 70.06, 112.04, 118.05, 122.69, 131.15, 131.50, 135.41, 138.04, 164.34. HRMS ($[M]^+ - 15$ for $C_{11}H_{15}O^{120}Sn$): 283.0098. Calc.: 283.0145. GC–MS: 283 (79), 281 (58), 279 (35), 268 (0.5), 253 (4), 242 (9), 240 (6), 219 (17), 212 (6), 133 (100), 131 (8), 120 (2), 105 (4), 91 (32), 69 (7).

4.5.3. *Trimethyl-(1-phenoxy-allyl)-stannane (**8a**)*

This compound was synthesized from (1-chloro-allyloxy)-benzene (vide supra) and Me_3Sn^- in HMPA, in 50% yield (determined by GC), according to the following general procedure: To an HMPA solution of sodium trimethyltin (4.7 mmol in 2 ml of solvent) prepared as described above, (1-chloro-allyloxy)-benzene (2.4 mmol dissolved in 1 ml of HMPA) was slowly introduced by syringe, and the mixture was left stirring to react for 48 h at room temperature (r.t.) in the dark. The reaction was worked up as usual, and the crude was chromatographed over silca-gel column chromatography, using CH_2Cl_2:petroleum ether (5:95) as eluants (39% isolated yield), and characterized by ^{1}H-NMR, GC–MS, and EIHRMS data as follow: ^{1}H-NMR (in $CDCl_3$) δ (ppm): 0.26 (s, 9H), 3.96 (dt, 1H), 5.45 (tq, 2 H), 5.35 (cplx. m, 1H), 6.80 (cplx. m, 2H), 6.90 (cplx.m, 1H), 7.28 (cplx.m, 2H). HRMS ($[M]^+ - 15$ for $C_{11}H_{15}O^{120}Sn$): 283.0160. Calc.: 283.0145. GC–MS (m/z, %): 298 ($[M]^{+\cdot}$, 5), 283 (25), 281 (20), 279 (15), 253 (2), 213 (3), 166 (15), 165 (100), 163 (86), 161 (51), 150 (5), 133 (23), 117 (4), 115 (3), 105 (28), 94 (6), 77 (18), 51 (15).

4.5.4. *Compound **8b***

HRMS ($[M]^+ - 15$ for $C_{11}H_{15}O^{117}Sn$): 283.0145. Calc.: 283.0166.

4.5.5. *(2-Allyloxy-phenyl)-trimethyl-silane (**11**)*

The compound [21] was isolated as indicated above, and characterized by ^{1}H-NMR and ^{13}C-NMR, and GC–MS data as follow: ^{1}H-NMR (in CD_3COCD_3) δ (ppm): 0.35 (ss, 9 H), 4.68 (dt, 2H, $J = 1.46$, 3.3, 5.5 Hz), 5.33 (dq, 1H, $J = 1.46$, 3.3, 12.1 Hz), 5.51 (dq, 1H, $J = 1.82$, 3.7, 17.2 Hz), 6.18 (double quintet, 1H, 17.2Hz, 5.1 Hz, $J = 12.1$), 7.01 (cplx.m, 2H), 7.41 (cplx.m, 2H). ^{13}C-NMR (in $CDCl_3$) δ (ppm): −0.92, 68.59, 110.47, 117.08, 120.53, 128.13, 130.61, 133.52, 135.02, 163.25. GCMS (m/z, %): 206 ($[M]^+$, 45), 191 (95), 175 (17), 163 (96), 151 (81), 150 (39), 149 (71), 135 (100), 15 (21), 91 (63), 73 (31), 59 (21), 41 (31).

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