

Review

Recent Advances in the Substitution Reactions of Triorganylstannyl Ions with Aromatic Compounds by the $S_{RN}1$ Mechanism. Synthetic Applications

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Abstract: A review on the reactions of triorganyl stannyl ions with haloarenes is presented. Emphasis on the synthetic applications of the resulting triorganyl stannyl aryl compounds is made, with their inherent potential to build large molecules through the $S_{RN}1$ sequence, i.e. $ArX \rightarrow ArSnR_3 \rightarrow ArAr$, which can be iteratively repeated when appropriately substituted substrates are chosen.

Keywords: stannyl anions, $S_{RN}1$, Stille reactions.

Introduction

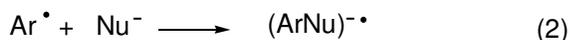
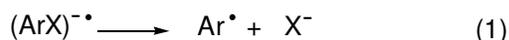
The reaction of triorganostannyl ions as nucleophiles with haloarenes has long been known, and the products obtained depend on the nucleophile, solvent, and on the reaction conditions. Thus, the reactions of sodium trimethyltin ($NaSnMe_3$) with halobenzenes (chloro-, bromo- and iodo-) in tetraglyme as solvent afford phenyltrimethyltin (Me_3SnPh) and variable amounts of reduction product benzene along with diphenyldimethyltin (Ph_2SnMe_2) and tetramethyltin ($SnMe_4$). From trapping experiments and solvent effects it has been proposed that the reaction occurs by a halogen metal exchange (HME) mechanism in a solvent cage. The formation of secondary products, Ph_2SnMe_2 and $SnMe_4$, has been ascribed to the decomposition of $NaSnMe_3$ into $NaMe$ and dimethylstannylene [1]. The reaction of *o*-dibromobenzene with $NaSnMe_3$ affords the disubstitution product *o*-bis(trimethylstannyl) benzene in 42% yield. In this reaction, the intermediate *o*-bromophenyl anion, can decompose into benzyne, which can then be trapped with furan to render the corresponding Diels-Alder adduct [2].

The reaction of *o*-, *m*- and *p*-bromotoluenes with $LiSnBu_3$ in THF as solvent affords the expected

substitution product, but when *p*-chloro and *p*-fluorotoluenes are used as substrates, *cine* substitution products are obtained, indicating that a benzyne mechanism operates. When radical traps are added, *cine* substitution products increase in yields, and in the presence of Li metal, the yields of *ipso* products are enhanced. According to these results, the reaction should proceed, at least in part, by a radical mechanism [3]. No light stimulation was employed in these reactions.

There are several methods of synthesis for trialkylarylstannanes, typically by the reaction of aryl lithium or organomagnesium derivatives with trialkyltin halides. These reactions have the drawback that many substituents on the aromatic ring are incompatible with the formation of aryl lithium or organomagnesium derivatives [4]. We have described the photostimulated reactions of haloarenes with triorganylstannyl ions by the S_{RN}1 mechanism. These reactions afford good to excellent yields of the nucleophilic substitution products. Many substituents are compatible with the S_{RN}1 mechanism, such as CO₂⁻, CO₂R, CONR₂, RO-, -CN, R, aryl, NH₂, NR₂ and SO₂R. [5] Another approach is the palladium catalysis (Stille reaction) of aryl halides [6] or aryl triflates [7] with hexamethyl- and hexabutyl-distannanes. Bis(trimethylstannyl) arenes can also be synthesized by palladium catalysis; the yields of disubstitution products range from 40 to 60% [8]. There are few examples involving reactions of bis(trimethylstannyl) arenes and heteroarenes with aryl halides, which afford a double arylation by the palladium cross-coupling reaction. The examples known afford modest to good yields (6-85% yield) of double arylation [9,10,11].

The S_{RN}1 mechanism is a chain process, whose main steps are presented in Scheme 1.



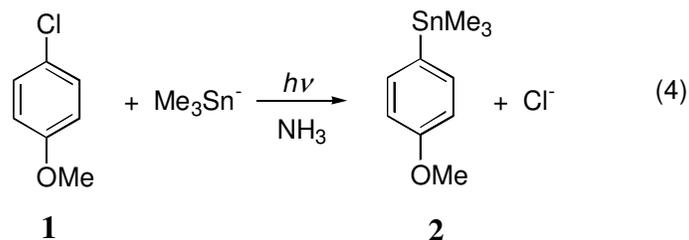
Scheme 1.

Overall, eqs. 1-3 depict a nucleophilic substitution (eq. 1,3) in which radicals and radical anions are intermediates. 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 often be induced by light stimulation.

In this review we present the results of the reactions of organotin nucleophiles with aryl halides by the S_{RN}1 mechanism and their synthetic applications. Reactions are compiled in Tables 1 and 2.

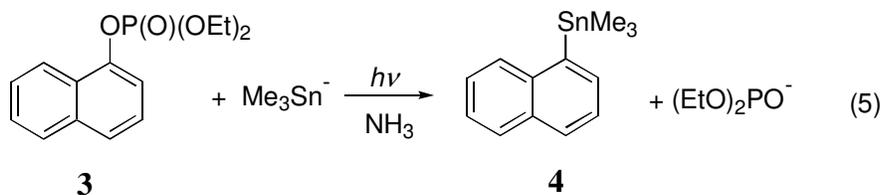
2. Me₃Sn⁻ Ions as Nucleophile

Trimethylstannyl anion (Me₃Sn⁻) is prepared in liquid ammonia through the reaction of Me₃SnCl with Na metal. *p*-Chloroanisole (**1**) does not react with Me₃Sn⁻ ions in the dark after 1 h, but upon irradiation (Hg lamp, 366 nm, 1 h), substitution product **2** was obtained in ca. 100% yield (Table I) (eq. 4). The photostimulated reaction is inhibited by *p*-dinitrobenzene, a well-known inhibitor of S_{RN}1 processes [12].



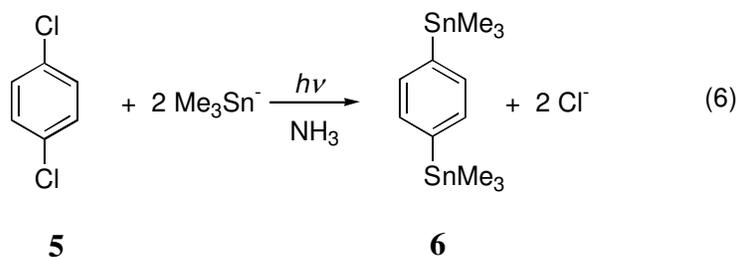
Conversely, *p*-bromoanisole in the presence of Me_3Sn^- ions affords exclusively anisole in the dark. This reaction proceeds by a HME, with a very fast protonation of the *p*-anisyl anion by liquid ammonia, anisole being the only product obtained. Bromides and iodides will likely react by a HME reaction faster than by the $\text{S}_{\text{RN}}1$ mechanism. When 2-chloroquinoline is allowed to react in the dark with Me_3Sn^- ions, low yields of the respectively-substituted product are obtained, a reaction which is inhibited by *p*-DNB and accelerated by light (96%). Other examples are indicated in Table I.

Aryldiethylphosphates are as good leaving groups as chlorines, and they both react with amide ions, NH_2^- , to afford substitution products by the $\text{S}_{\text{RN}}1$ mechanism [13]. The synthesis of aryl trimethylstannanes from phenols through aryldiethylphosphates has recently been reported to proceed in high yields in liquid ammonia. For instance, the photostimulated reaction of **3** with Me_3Sn^- ions affords the substitution product **4** in 93% yield (eq. 5) [14]. These reactions do not occur in the dark.

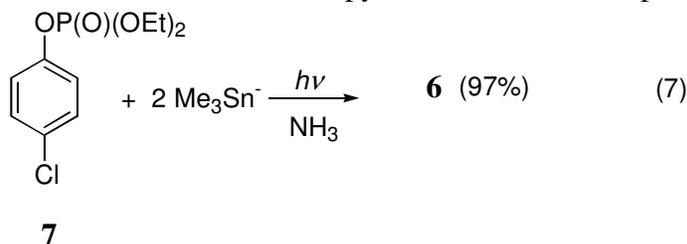


Phenyltrimethyl ammonium salts also react with Me_3Sn^- ions in liquid ammonia to give the substitution product in high yields (Table I) [15].

When the aromatic substrate bears two leaving groups, such as *p*-dichlorobenzene (**5**), disubstitution product **6** is isolated in 88% yield (eq. 6). The monosubstitution product is not an intermediate in these reactions.



With two different leaving groups, such as in **7**, compound **6** is obtained in excellent yields as well (eq. 7). Substrates such as 2,5-, 2,6- and 3,5- dichloropyridines afford the respective disubstitution products



in 80-86% yields [16] (Table I). There is a report where several chloro, bromo, dichloro and dibromo pyridines and quinolines react with Me_3Sn^- ions in dimethoxyethane to render the mono and disubstitution products in 60-88% yields. There is no photostimulation in these reactions, and no information is provided about the mechanism [17].

We have found that the photostimulated reaction of 1,3,5-trichlorobenzene **8** in the presence of an excess of Me_3Sn^- ions affords 71% of the trisubstitution product **9** (eq. 8).

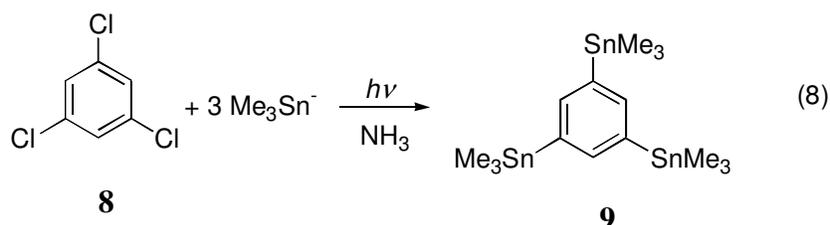


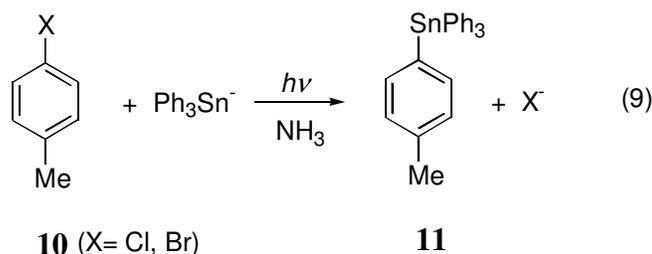
Table 1. Reactions of Me_3Sn^- ions with aromatic compounds in liquid ammonia by the $\text{S}_{\text{RN}}1$ mechanism.

<u>Substrate</u>	<u>Conditions</u>	<u>Products (Yields %)</u>	<u>Ref.</u>
<i>p</i> -MeOC ₆ H ₄ Cl	Dark, 1 h	<i>p</i> -MeOC ₆ H ₄ SnMe ₃ (0)	12
<i>p</i> -MeOC ₆ H ₄ Cl	<i>hν</i> , 1 h	<i>p</i> -MeOC ₆ H ₄ SnMe ₃ (100)	12
<i>p</i> -MeOC ₆ H ₄ Cl	<i>hν</i> , 1 h, <i>p</i> -DNB	<i>p</i> -MeOC ₆ H ₄ SnMe ₃ (0)	12
<i>p</i> -MeOC ₆ H ₄ OP(O)(OEt) ₂	<i>hν</i> , 1 h	<i>p</i> -MeOC ₆ H ₄ SnMe ₃ (81)	14
PhNMe ₃ I	<i>hν</i> , 1 h	PhSnMe ₃ (98)	15
<i>p</i> -NCC ₆ H ₄ Cl	<i>hν</i> , 1 h	<i>p</i> -NCC ₆ H ₄ SnMe ₃ (85)	16
1-C ₁₀ H ₇ Cl ^a	<i>hν</i> , 1 h	1-C ₁₀ H ₇ SnMe ₃ (90)	12
1-C ₁₀ H ₇ OP(O)(OEt) ₂ ^a	<i>hν</i> , 1 h	1-C ₁₀ H ₇ SnMe ₃ (93)	14
2-C ₅ H ₄ NCl ^b	<i>hν</i> , 1.5 h	2-C ₅ H ₄ NSnMe ₃ (88)	16
2-C ₉ H ₆ NCl ^c	Dark, 1 h	2-C ₉ H ₆ NSnMe ₃ (65)	12
2-C ₉ H ₆ NCl ^c	Dark, 1 h, <i>p</i> -DNB	2-C ₉ H ₆ NSnMe ₃ (12)	12
2-C ₉ H ₆ NCl ^c	<i>hν</i> , 1 h	2-C ₉ H ₆ NSnMe ₃ (96)	12
<i>o</i> -Cl ₂ C ₆ H ₄	<i>hν</i> , 1 h	<i>o</i> -(Me ₃ Sn) ₂ C ₆ H ₄ (58)	16
<i>m</i> -Cl ₂ C ₆ H ₄	<i>hν</i> , 1.5 h	<i>m</i> -(Me ₃ Sn) ₂ C ₆ H ₄ (90)	16
<i>p</i> -Cl ₂ C ₆ H ₄	<i>hν</i> , 1 h	<i>p</i> -(Me ₃ Sn) ₂ C ₆ H ₄ (88)	12
<i>p</i> -ClC ₆ H ₄ OP(O)(OEt) ₂	<i>hν</i> , 1 h	<i>p</i> -(Me ₃ Sn) ₂ C ₆ H ₄ (97)	14
<i>p</i> -C ₆ H ₄ [OP(O)(OEt) ₂] ₂	<i>hν</i> , 1 h	<i>p</i> -(Me ₃ Sn) ₂ C ₆ H ₄ (95)	14
2,5-C ₅ H ₃ NCl ₂ ^b	2 h	2,5-C ₅ H ₃ N(Me ₃ Sn) ₂ (88)	16
3,5-C ₅ H ₃ NCl ₂ ^b	<i>hν</i> , 2 h	3,5-C ₅ H ₃ N(Me ₃ Sn) ₂ (80)	16
2,6-C ₅ H ₃ NCl ₂ ^b	<i>hν</i> , 1.5 h	2,6-C ₅ H ₃ N(Me ₃ Sn) ₂ (86)	16
1,3,5-Cl ₃ C ₆ H ₃	<i>hν</i> , 1 h	1,3,5-(Me ₃ Sn) ₃ C ₆ H ₃ (71)	16

^aNaphthyl. ^bPyridyl. ^cQuinolyl.

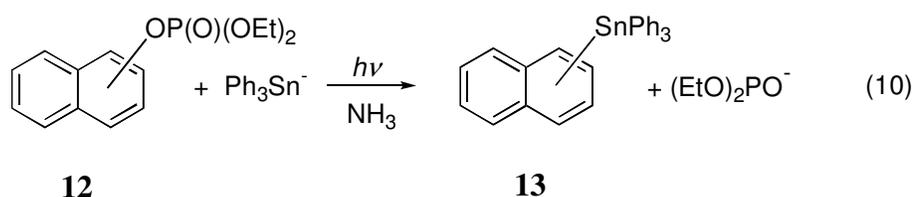
3. Ph_3Sn^- Ions as Nucleophile

Triphenylstannyl ion (Ph_3Sn^-) was prepared either from reaction of Ph_3SnCl or $\text{Ph}_3\text{SnSnPh}_3$, with Na metal in liquid ammonia. *p*-Chloro or *p*-bromotoluenes **10** do not react with Ph_3Sn^- ions in the dark in liquid ammonia as solvent, but upon irradiation, substitution product **11** is obtained in good yields (eq. 9) (Table 2). *p*-Chloroanisole, under irradiation in DMSO, affords only 30% yield of the substitution product.



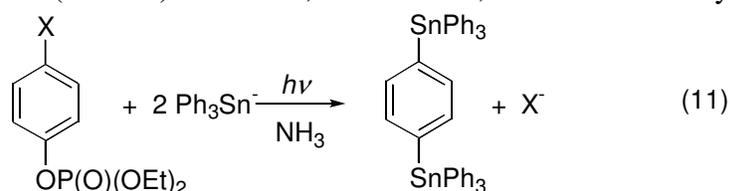
However, when *p*-iodotoluene and *p*-iodoanisole are utilized as substrates, a fast HME reaction takes place, affording the reduced product in the dark. Upon irradiation, low yields of substitution products are obtained by the $\text{S}_{\text{RN}}1$ mechanism, which competes with the HME reaction (Table 2). In DMSO as solvent, only the HME reaction is observed.

1-Chloro and 1-bromo naphthalenes afford good yields of the substitution product when irradiated in liquid ammonia in the presence of Ph_3Sn^- ions. In DMSO as solvent, 1-chloronaphthalene affords good yields of substitution, i.e.: 1-(triphenylstannyl)naphthalene, however, the bromo derivative gives only the HME reaction. From these results it is concluded that the bromo derivatives react mainly by HME reaction in DMSO, but good yields of substitution products are obtained in liquid ammonia. 1- and 2-Naphthyldiethyl-phosphates **12** render excellent yields of substitution products **13** when irradiated in liquid ammonia in the presence of Ph_3Sn^- ions (eq. 10).



When *p*-dichlorobenzene is allowed to react with Ph_3Sn^- ions under photostimulation in liquid ammonia or DMSO, good yields of the disubstitution product are obtained (60% or 90% respectively.) When *p*-dibromobenzene is utilized as substrate, there is a fast HME reaction to afford PhBr. Upon irradiation, the disubstitution product, i.e.: *p*-bis(triphenyltin) benzene, is obtained in only 22% yield, along with tetraphenyltin, which arises from reaction of PhBr with Ph_3Sn^- ion.

p-Dibromobenzene reacts with Ph_3Sn^- ions in the absence of photostimulation to afford 96% yield of PhBr. In the case of ArI as substrates and Ph_3Sn^- ions as nucleophile, the predominant reaction is the HME in liquid ammonia (Table 2). However, substrate **14**, affords excellent yields of the disubstitution



product **15** (eq. 11).

Heterocycles afford high yields of substitution products when the irradiations are conducted in the presence of Ph_3Sn^- ions in liquid ammonia or DMSO. Thus, in DMSO, 2- and 3-chloropyridines afford, the substitution products in 82% and 93% yields respectively; and in liquid ammonia, 2-chloroquinoline furnishes 2-(triphenyltin)quinoline in 80% yield (Table 2).

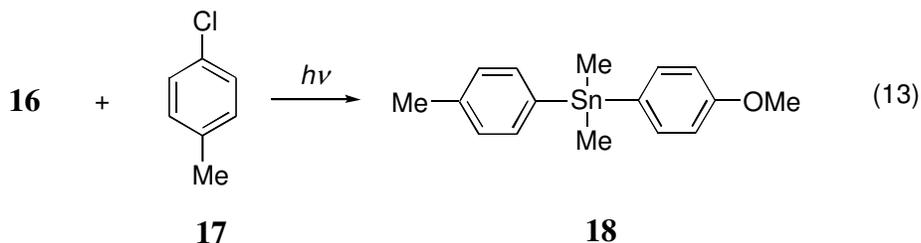
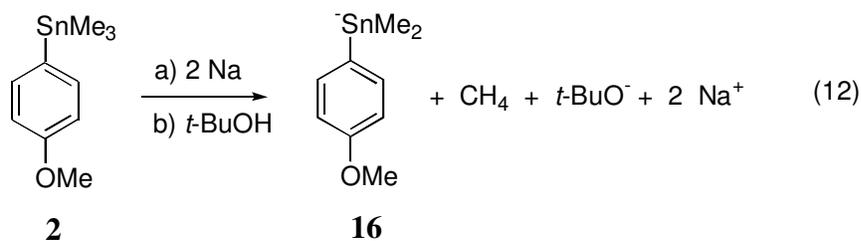
Table 2. Reactions of Ph_3Sn^- ions with aromatic compounds by the $\text{S}_{\text{RN}}1$ mechanism

Substrate	Conditions	Products (Yield %)	Ref.
<i>p</i> -MeC ₆ H ₄ Cl	Dark, NH ₃ , 1 h	<i>p</i> -MeC ₆ H ₄ SnPh ₃ (0)	12
<i>p</i> -MeC ₆ H ₄ Cl	<i>hν</i> , NH ₃ , 2 h	<i>p</i> -MeC ₆ H ₄ SnPh ₃ (75)	12
<i>p</i> -MeOC ₆ H ₄ Cl	<i>hν</i> , DMSO, 24 h	<i>p</i> -MeOC ₆ H ₄ SnPh ₃ (30)	[18]
<i>p</i> -MeC ₆ H ₄ Br	<i>hν</i> , NH ₃ , 1 h	<i>p</i> -MeC ₆ H ₄ SnPh ₃ (62)	12
<i>p</i> -MeC ₆ H ₄ I	<i>hν</i> , NH ₃ , 1 h	<i>p</i> -MeC ₆ H ₄ SnPh ₃ (38)	12
<i>p</i> -MeOC ₆ H ₄ I	<i>hν</i> , NH ₃ , 1 h	<i>p</i> -MeOC ₆ H ₄ SnPh ₃ (20) ^a	12
1-C ₁₀ H ₇ Cl ^b	<i>hν</i> , NH ₃ , 3 h	1-C ₁₀ H ₇ SnPh ₃ (80)	12
1-C ₁₀ H ₇ Cl ^b	<i>hν</i> , DMSO, 4 h	1-C ₁₀ H ₇ SnPh ₃ (72)	18
1-C ₁₀ H ₇ Br ^b	<i>hν</i> , NH ₃ , 1 h	1-C ₁₀ H ₇ SnPh ₃ (75) ^a	12
1-C ₁₀ H ₇ OP(O)(OEt) ₂ ^b	<i>hν</i> , NH ₃ , 4 h	1-C ₁₀ H ₇ SnPh ₃ (100) ^c	14
2-C ₁₀ H ₇ OP(O)(OEt) ₂ ^b	<i>hν</i> , NH ₃ , 6 h	2-C ₁₀ H ₇ SnPh ₃ (100) ^c	14
2-C ₅ H ₄ NCl ^d	<i>hν</i> , DMSO, 6 h	2-C ₅ H ₄ NSnPh ₃ (82)	18
3-C ₅ H ₄ NCl ^d	<i>hν</i> , DMSO, 6 h	3-C ₅ H ₄ NSnPh ₃ (93)	18
2-C ₉ H ₆ NCl ^e	<i>hν</i> , NH ₃ , 1 h	2-C ₉ H ₆ NSnPh ₃ (80)	12
<i>p</i> -C ₆ H ₄ Cl ₂	<i>hν</i> , NH ₃ , 3 h	<i>p</i> -C ₆ H ₄ [SnPh ₃] ₂ (69)	12
<i>p</i> -C ₆ H ₄ Cl ₂	<i>hν</i> , DMSO, 6 h	<i>p</i> -C ₆ H ₄ [SnPh ₃] ₂ (90)	18
<i>p</i> -C ₆ H ₄ Br ₂	<i>hν</i> , NH ₃ , 1 h	<i>p</i> -C ₆ H ₄ [SnPh ₃] ₂ (22) ^a	12
<i>p</i> -BrC ₆ H ₄ OP(O)(OEt) ₂	<i>hν</i> , NH ₃ , 2 h	<i>p</i> -C ₆ H ₄ [SnPh ₃] ₂ (70) ^c	14
<i>p</i> -C ₆ H ₄ [OP(O)(OEt) ₂] ₂	<i>hν</i> , NH ₃ , 1.5 h	<i>p</i> -C ₆ H ₄ [SnPh ₃] ₂ (100) ^c	14

^aOnly reduction in DMSO. ^bNaphthyl. ^cAfter the irradiation, Na metal was added. ^dPyridyl. ^eQuinoly.

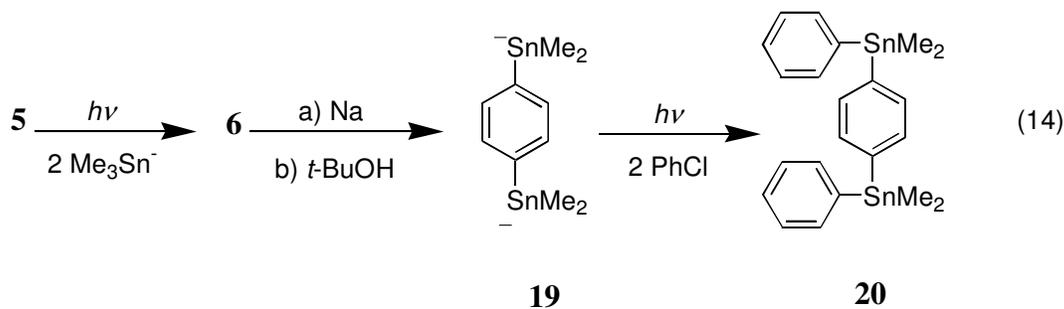
4. Other Tin-derived Nucleophiles

When *p*-anisyltrimethyltin **2** reacts with sodium metal in liquid ammonia, the Sn-Me bond is cleaved to render nucleophile **16**, after neutralization of the generated amide ions with *t*-butyl alcohol (eq. 12) [19]. This result is consistent with the bond dissociation energy difference between the tin-phenyl bond (347 kJ mol⁻¹) [20] and the tin-methyl bond (259-272 kJ mol⁻¹) [20, 21]. Nucleophile **16** was then allowed to react with *p*-chlorotoluene **17** under irradiation to afford substitution product **18** in almost quantitative yields (eq. 13).

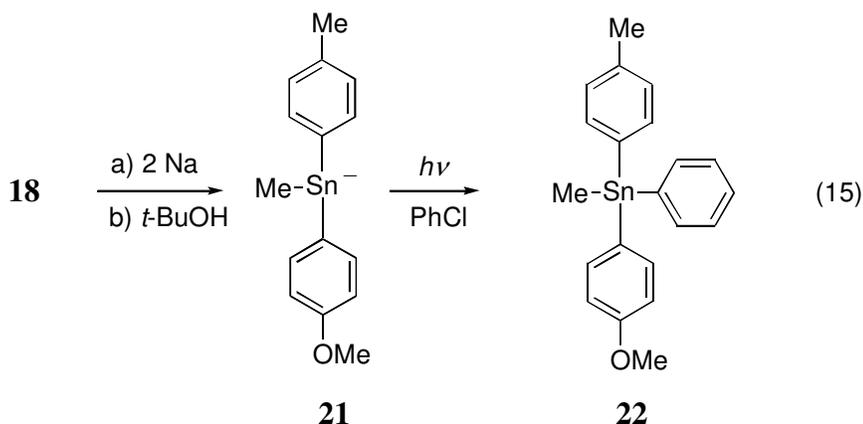


Product **18** was also obtained in a one-pot fashion starting from Me_3Sn^- and *p*-chloroanisole under photostimulation. Intermediate product **2** was not isolated, but treated *in situ* with Na metal to afford nucleophile **16**, which by a subsequent photostimulated reaction in the presence of **17** rendered product **18** in 89% overall yield.

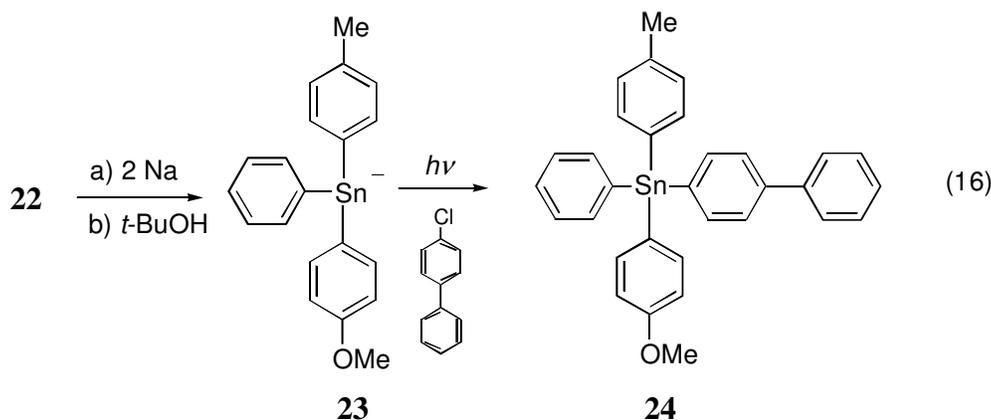
The photostimulated reaction of *p*-dichlorobenzene **5** with Me_3Sn^- ions in liquid ammonia affords the disubstitution product (**6**) (eq. 6). When this product is treated *in situ* first with Na metal and then with *t*-BuOH, dianion **19** is obtained, which upon addition of PhCl and ulterior irradiation (90 min) affords product **20** in a one-pot process (70%) [16] (eq. 14).



When **18** is treated with Na metal in liquid ammonia under the same reaction conditions as those employed above, nucleophile **21** is formed. Addition of PhCl followed by irradiation generates product **22** in 31% yield (eq. 15). The overall yield is significantly reduced in this case owing to the presence of products arising from some tin-aryl bond fragmentation.



When **22** is further treated with Na metal in liquid ammonia following the same procedures as utilized to form **16** or **21**, nucleophile **23** is obtained. Upon photostimulation of **23** in the presence of 4-chlorobiphenyl, product **24**, a chiral aromatic organostannyl compound, is obtained in 25% yield (eq. 16).



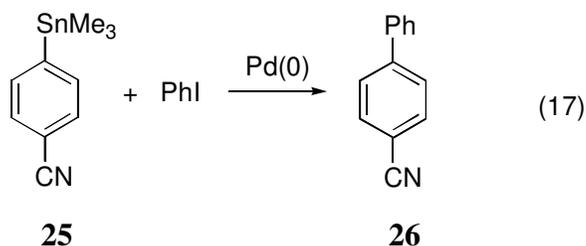
As mentioned previously, both alkyl-Sn and aryl-Sn bonds can fragment in the presence of Na metal in liquid ammonia, decreasing the selectivity of the fragmentation path. Selectivity towards alkyl-Sn bond fragmentation at the expense of aryl-Sn bond scission can be improved by exchanging the methyl group for another alkyl group with lower Sn-C bond dissociation energy. In fact, the cleavage of either *n*-butyltriphenyl tin (BDE (Sn-Bu) = 209 kJ mol⁻¹) [20] or benzyltriphenyltin (BDE (Sn-benzyl) = 163 kJ mol⁻¹) [22] leads exclusively to Sn-alkyl bond fragmentation.

5. Synthetic Applications

Aryltrialkyl stannanes are valuable intermediates in organic synthesis, and the fact that they can be easily synthesized through the S_{RN}1 mechanism, opens up important synthetic routes to different reaction schemes. Halodemetalation of aryltrialkyl stannanes has been one such example [23]. The reaction of Me₃Sn⁻ ions with aryl chlorides with ulterior addition of iodine in CHCl₃ has been used to obtain aryl iodides from aryl chlorides in very good yields [17].

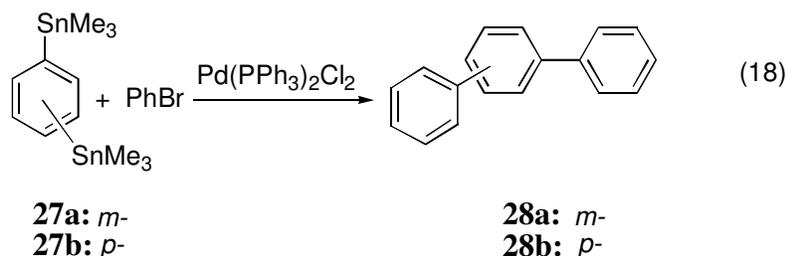
For over a decade, the palladium-catalyzed cross-coupling of organotin compounds with carbon electrophiles, known as the Stille reaction [24], has been a very important tool in organic synthesis [25]. The reaction of *p*-cyanophenyltrimethylstannane **25** [26] with PhI and Pd(PPh₃)₂Cl₂ as catalyst in DMF (80°C, 3

h), affords the coupling product 4-biphenylcarbonitrile **26** in 81% yield (eq. 17) [27].



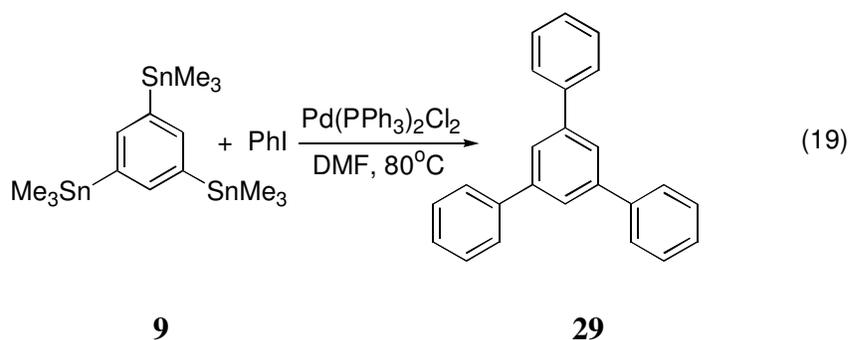
The synthesis of the stannane and the Stille reaction were carried out in a one-pot procedure consisting of irradiating a liquid ammonia solution of *p*-chlorobenzonitrile and NaSnMe₃, followed by quenching of the reaction by MeI [28]. The ammonia was allowed to evaporate, and the residue was taken up in DMF when PhI, and Pd(PPh₃)₂Cl₂ were added. Product **26** was obtained in 63% yield.

As shown before, high yields of disubstitution products can be obtained by the S_{RN}1 mechanism from dichloro arenes and heteroarenes. For instance, when distannane **27a** is heated at 80°C in the presence of PhBr and Pd(PPh₃)₂Cl₂ in DMF, *m*-terphenyl **28a** is obtained in 97% isolated yield (eq. 18). Under the same reaction conditions, the distannane **27b** affords *p*-terphenyl **28b** in 90% isolated yield.

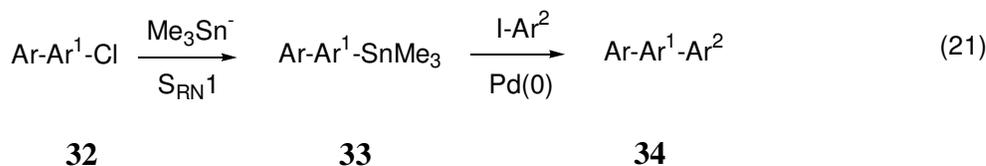
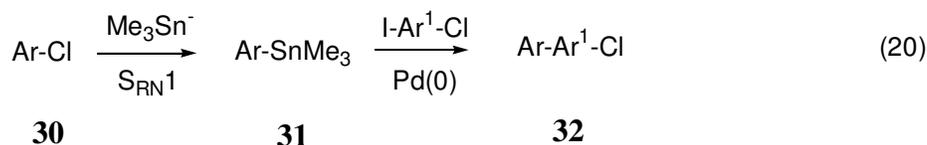


The one-pot photoreaction in liquid ammonia of *m*-dichlorobenzene and NaSnMe₃ followed by quenching with MeI, evaporation of the ammonia, and redissolving in DMF in the presence of PhBr and Pd(PPh₃)₂Cl₂ as described above, leads to product **28a** in 76% yield. Following the same procedure but using *p*-dichlorobenzene, product **28b** is obtained in 71% yield. Reaction of 2,6-di(trimethylstannyl)pyridine with PhI and Pd(PPh₃)₂Cl₂ affords diphenylated pyridine (72%), along with 2-phenylpyridine (25%). In the one-pot fashion, substrate 2,6-dichloropyridine rendered the diphenylated product in 60% overall yield.

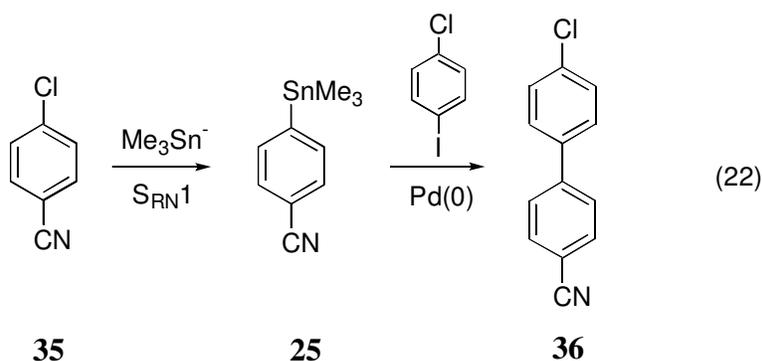
A triphenylation reaction was conducted utilizing the tristannane **9**. Upon reaction of **9** with PhI in the presence of catalytic Pd(PPh₃)₂Cl₂, triphenylated product **29** was obtained in 89% yield (eq. 19). In the one-pot procedure, 1,3,5-trichlorobenzene affords **29** in 61% isolated yield.



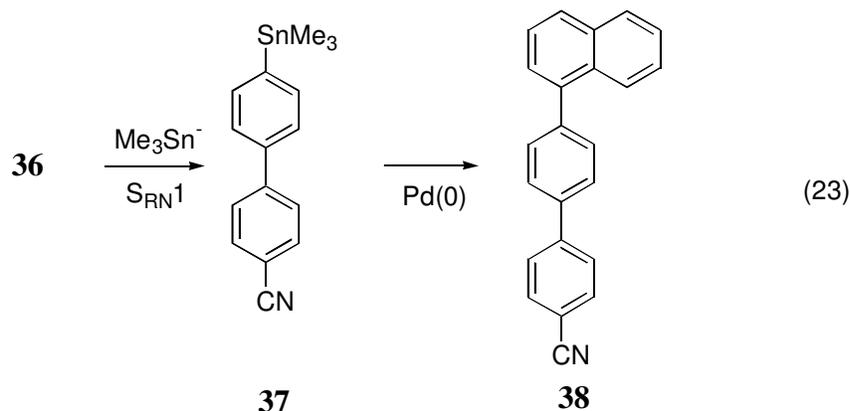
The fact that chloroarenes **30** react with Me_3Sn^- ions under photostimulation to form aryltrimethyl stannanes **31**, and that in the Pd-catalyzed Stille reaction with stannanes the reactivity of iodoarenes is much greater than that of chloroarenes, a substrate bearing both leaving groups, Cl and I, will react by the C-I bond (product **32**, eq. 20) and not by the C-Cl bond, in a Stille-type reaction. This will allow the remainder leaving group, Cl, to react later in another $\text{S}_{\text{RN}}1$ -type reaction to form an organostannyl intermediate (product **33**) which can ultimately furnish product **34** (eq. 21) by a palladium catalyzed cross-coupling.



The above sequence, $\text{S}_{\text{RN}}1$ reaction-Pd catalyzed reaction- $\text{S}_{\text{RN}}1$ reaction-Pd catalyzed reaction was investigated in our laboratory in order to foster a methodology to build large molecules. The photo-stimulated reaction of *p*-chlorobenzonitrile **35** with Me_3Sn^- ion affords the stannane **25**, which by a Pd (0)-catalyzed reaction with *p*-chloriodobenzene furnishes product **36** in 94% yield (eq. 22). [15]



By a photostimulated reaction of Me_3Sn^- ion in the presence of **36**, stannane **37** is obtained in 94% yield. A second Pd(0)-catalyzed reaction with 1-iodonaphthalene renders product **38** in 93% yield (eq. 23).



All these results indicate that the $S_{RN}1$ mechanism is an excellent method to obtain stannanes by the photostimulated reactions of mono-, di- and trichloro arenes with Me_3Sn^- in liquid ammonia. The stannanes thus obtained can be arylated by further reaction with bromo or iodoarenes through palladium-catalyzed reactions. If the $Pd(0)$ -catalyzed reaction is performed with a chloriodoarene substrate, the product obtained can be further arylated by a consecutive $S_{RN}1$ -Stille reaction.

6. Conclusions and Summary Remarks

The $S_{RN}1$ reactions of trimethylstannyl and triphenylstannyl anions with haloarenes are quite versatile. The reaction products are of prominent synthetic relevance and can be utilized as intermediates in important reactions, such as the Stille reaction. Thus, the $S_{RN}1$ mechanism affords triorganyl stannyl aromatic compounds which otherwise would be synthesized by routes which employ harsher reaction conditions. The sequence $S_{RN}1$ - Pd -catalysis is a powerful synthetic tool, and the scope of the reaction is unlimited owing to the nature of the sequence, i.e. $ArX \rightarrow ArSnR_3 \rightarrow ArAr$, which can be iteratively repeated when appropriately substituted substrates are chosen.

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Samples Availability: Not applicable.