Trimethylstannylation of mono- and dichloroarenes by the $S_{RN}1$ mechanism in liquid ammonia[†]

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ABSTRACT: The photostimulated reaction of methyl 2,5-dichloro benzoate (**1**) or methyl 3,6-dichloro-2-methoxy benzoate (**7**) with $^-SnMe_3$ ions give good yields of the disubstitution products by the $S_{RN}1$ mechanism in liquid ammonia. Conversely, in dark conditions, substrate **1** reacts with $^-SnMe_3$ ions to afford the mono-substitution products by the $S_{RN}1$ mechanism. On the other hand, substrate **7** reacts with $^-SnMe_3$ ions in dark conditions to give mono-reduced product probably by a halogen metal exchange reaction. In addition, the photostimulated reaction of 2-chloro-N^4-ethyl-N^6-isopropyl-1,3,5-triazin-4,6-diamine (Atrazine, **11**) with $^-SnMe_3$ ions affords the reduced and substitution products in liquid ammonia-DMSO as co-solvent. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: $S_{RN}1$ reactions; radicals; $^-SnMe_3$ ions; chloroarenes; Disugran; Atrazine
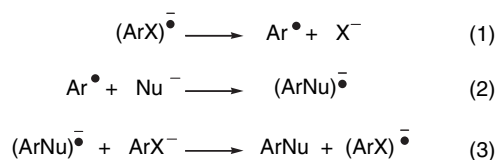
INTRODUCTION

The radical nucleophilic substitution, or $S_{RN}1$ reaction, is a chain process with radicals and radical anions as intermediates, 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.

This chain process requires an initiation step. The most frequently used methods for initiation are chemical initiation by alkali metals in liquid ammonia, electrochemical initiation at a cathode, and photoinitiation. In a few systems a thermal (spontaneous) initiation is observed. The propagation steps of an $S_{RN}1$ mechanism are presented in Scheme 1.

The wide variety of nucleophiles that can be used, the great functional group tolerance and the fact that many carbon–carbon and carbon–heteroatom bonds can be obtained, makes the $S_{RN}1$ reaction a powerful synthetic tool.

The reaction of triorganostannyl ions as nucleophiles with aryl halides has long been known, and the products obtained depend on the leaving group, the nucleophile,

$$(ArX)^{\bar{\bullet}} \longrightarrow Ar^{\bullet} + X^- \qquad (1)$$

$$Ar^{\bullet} + Nu^- \longrightarrow (ArNu)^{\bar{\bullet}} \qquad (2)$$

$$(ArNu)^{\bar{\bullet}} + ArX^- \longrightarrow ArNu + (ArX)^{\bar{\bullet}} \qquad (3)$$

Scheme 1

solvent, and on the reaction conditions. We have described the photostimulated reactions of trimethylstannyl ions ($^-SnMe_3$) with several chloroarenes in liquid ammonia that afford $ArSnMe_3$ from very good to excellent yields (70–100%).[2] The fact that there is no reaction in the dark but only under irradiation, and that the photostimulated reactions are inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions, indicates that these reactions occur by the $S_{RN}1$ mechanism. These reactions are an alternative route to the synthesis of stannanes, avoiding the use of Grignard reagents or organolithium compound. These reactions can also be carried out in DMSO as solvent under irradiation.[3]

The $S_{RN}1$ reactions of dihaloarenes with nucleophiles afford either the monosubstitution or disubstitution product, depending on the structure of the substrate, and the nature of the nucleofugal group or the nucleophile. We found that several dichloroarenes give the disubstitution product in high yields [Eqn (4)]. Also, dichloropyridines react to afford disubstituted products. The photostimulated reaction of 1,3,5-trichlorobenzene in the presence of an excess of $^-SnMe_3$ ions affords 71% of the trisubstitution product.[4]

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(4)

58-96%
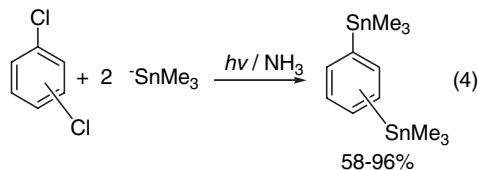
Mono- and distannanes can also be formed from diethylaryl phosphonates[5,6] or aryltrimethyl ammonium salts[7,8] by the $S_{RN}1$ mechanism. It has been demonstrated that haloarenes react in diglyme with $^-SnMe_3$ ions under irradiation by the $S_{RN}1$ mechanism.[8]

A simple method to synthesize five-substituted resorcinol derivatives has been published. 1-Chloro-3,5-dimethoxybenzene reacts with the $^-SnMe_3$ ions in liquid ammonia under irradiation to afford substitution product in good yields [Eqn (5)].[9]

(5)

80%
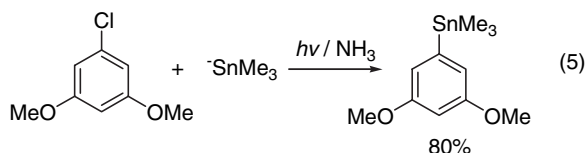
The $S_{RN}1$ reactions of $^-SnMe_3$ ions with haloarenes are quite versatile. The reaction products are of prominent synthetic relevance and can be utilized as intermediates in important reactions, such as the Stille reaction.[8,9,10] A sequence of $S_{RN}1$ followed by a cross-coupling reaction catalyzed by Pd(0) has been developed to obtain polyphenylated compounds as shown in Eqn (6). Following the same procedure, 1,3,5-triphenylbenzene was obtained in 61% isolated yield from 1,3,5-trichlorobenzene in a one-pot procedure.[10]

(6)

Z= CH, *m*-: 76%
Z= CH, *p*-: 71%
Z= N, 2,6-: 60%
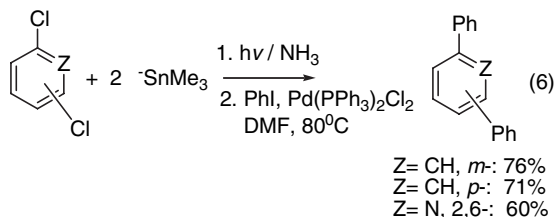
Although dehalogenation by a halogen metal exchange (HME) takes place with iodoarenes and 2- and 3-chlorothiophene, good yields of substitution are found with 2- and 3-chloropyridines in DMSO.[3]

2-chloro-N^4-ethyl-N^6-isopropyl-1,3,5-triazin-4,6-dia-mine (known as Atrazine) or 3,6-dichloro-2-methoxy benzoic acid (known as Dicamba) are among the most widely used chlorinated herbicides in different countries. These compounds are relatively stable under natural conditions and have become prominent contaminants in soil and hydrologic systems.

It was previously reported that chloro-s-triazine was rapidly dechlorinated in water by polysulfides, and the

reaction was assumed to be aromatic nucleophilic substitution (S_NAr).[11] In another study, the effect of free radical inhibitors on the reaction rate of polysulfides was evaluated with the herbicides Atrazine, Simazine, and Cyanazine. The reaction was significantly inhibited by radical scavengers, such as oxygen and 1,4-benzoquinone, suggesting involvement of free radicals in the reactions. Spectral analysis of the reaction mixture using electron spin resonance showed that after the reaction, the free radical concentration in polysulfide solution substantially decreased. This evidence indicates that sulfur centered radicals may also be involved in the reaction, likely via the $S_{RN}1$ mechanism.[12]

In order to synthesize different substituted herbicides we decided to investigate the reaction of chloro-substituted herbicides with $^-SnMe_3$ ions by the $S_{RN}1$ mechanism in liquid ammonia. This approach provides a facile preparation of compounds bearing trimethylstannyl groups.

The synthesis of these stannyl derivatives is of great interest since this group is readily changed by electrophiles, generating a new C—C bond and increasing the synthetic value of these reactions.

RESULTS AND DISCUSSION

Reactions of methyl-2,5-dichlorobenzoate (1) with $^-SnMe_3$ ions in liquid ammonia

We studied methyl 2,5-dichlorobenzoate (**1**) as a model compound of certain chlorinated herbicides. It was found that **1** reacts with the $^-SnMe_3$ ions in liquid ammonia under irradiation to afford disubstitution product (**2**) and only trace of other substitution product (**3** and **4**). However, in the dark, **1** reacted with $^-SnMe_3$ ions to give the mono-substitution product **3** in 81% yield [Eqn (7)] (Table 1, experiments 1 and 2).

(7)
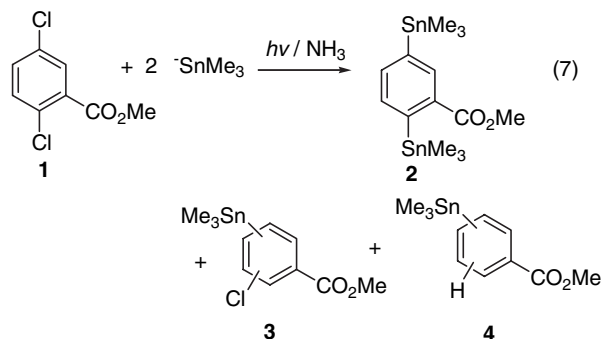
The dark reaction is not inhibited by *p*-DNB, but it is inhibited by radical scavengers as di-*ter*-butyl nitroxide (Table 1, experiments 3 and 4).

Moreover, the photostimulated reaction of **1** in excess with $^-SnMe_3$ ions rendered the products **2**, **3**, and **4** in 32%, 50%, and 10% yields, respectively. The fact that the monochloro substitution product **3** was formed

Table 1. Reaction of methyl 2,5-dichlorobenzoate (**1**) with $^-$SnMe$_3$ ions in liquid ammonia[a]

Experiment	**1**: $^-$SnMe$_3$ Ratio	Conditions (min)	Products (%)[b]
1	1:2.2	hv, (60)	**2** (99), **3** (traces), **4** (traces)
2	1:2.2	Dark (60)	**2** (2), **3** (81), **4** (<2)
3[c]	1:2.2	Dark (60)	**2** (6), **3** (76),[d] **4** (19)
4[e,f]	1:2.2	Dark (60)	**2** (—), **3** (9), **4** (1)
5[g]	1:1.1	hv, (60)	**2** (32), **3** (50), **4** (10)

[a] The concentration of substrate was 6.66×10^{-3} M. The concentration of nucleophile was 1.4×10^{-2} M, unless otherwise indicated.
[b] Quantified by GLC by the internal standard method with *p*-dibromobenzene as reference.
[c] *p*-DNB (20 mol%) was added.
[d] Together with hydrolyzed compound (ca. 1:1)
[e] Di-*ter*-butyl nitroxide (20 mol%) was added.
[f] Substrate and hydrolyzed substrate recovered in 61%.
[g] The concentration of nucleophile was 7×10^{-3} M.

indicates that this product is an intermediate in the reaction (Table 1, experiment 5).

These results suggest that **1** reacted by the S$_{RN}$1 mechanism, as shown in Scheme 2. When **1** receives one electron it gives a radical anion intermediate **1**$^{·-}$ which fragments at one of the C—Cl bond to give a radical intermediate **5**$^·$ [Eqn (8)]. This radical intermediate **5**$^·$
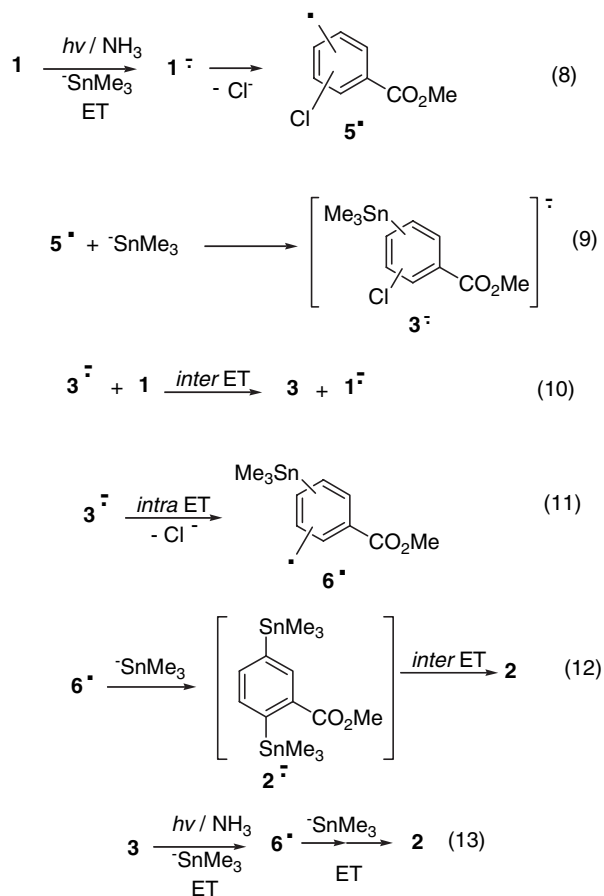
**Scheme 2**

reacts with $^-$SnMe$_3$ ions to form the radical anion **3**$^{·-}$ [Eqn (9)]. This radical anion **3**$^{·-}$ by intermolecular electron transfer (ET) to the substrate affords the monosubstitution product **3** [Eqn (10)], or by intramolecular ET to the second C—Cl bond forms the radical **6**$^·$ [Eqn (11)], which by coupling with $^-$SnMe$_3$ ions affords the radical anion of the disubstitution product **2**$^{·-}$, which by an ET reaction yields the disubstitution product **2** [Eqn (12)].

The fact that the monosubstitution product **3** is formed indicates that the intermolecular ET of the radical anion **3**$^{·-}$ [Eqn (10)] is faster than intramolecular ET to the σ^*MO of the C—Cl bond [Eqn (11)]. The intermediate stannane **3** further reacts by the S$_{RN}$1 mechanism with $^-$SnMe$_3$ ions to give finally the disubstitution product **2** [Eqn (13)].

Reactions of methyl 3,6-dichloro-2-methoxybenzoate (7) with $^-$SnMe$_3$ ions in liquid ammonia

Methyl 3,6-dichloro-2-methoxybenzoate (**7**), know as Disugran, is the methyl ester of the herbicide Dicamba. Substrate **7** reacts under photostimulation with $^-$SnMe$_3$ ions in liquid ammonia to give the substitution products **8** and **9**, and the reduced product **10** in 64%, 6%, and 3% yields, respectively [Eqn (14)]. This reaction affords principally **10** in the dark (Table 2, experiments 1 and 2).
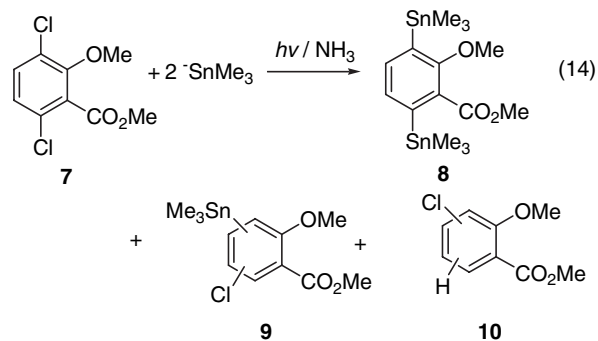
The photostimulated reaction was carried out in the presence of high excess of nucleophile in order to obtain the best conditions by the coupling reaction; however, the yield of the reduced product **10** increases. The fact that at higher concentration of the nucleophile, the reaction affords **10** and that the substitutions products (**8** and **9**) are formed in lower yields, suggest that the reduction process proceeds by a HME reaction [Eqn (15)] in competition with the S$_{RN}$1 reaction, with a very fast protonation of the aromatic anion **10**$^-$ formed by liquid ammonia (Table 2, experiment 3). The compound **7** reacts by an HME reaction faster compared to by the S$_{RN}$1 mechanism in dark condition.

Table 2. Reaction of methyl 3,6-dichloro-2-methoxybenzoate (**7**) with $^-$SnMe$_3$ ions in liquid ammonia[a]

Experiment	7 : $^-$SnMe$_3$ Ratio	Conditions (min)	Products (%)[b]
1[c]	1:3.2	*hv*, (60)	**8** (64), **9** (6), **10** (3)
2[c,d]	1:3.2	Dark (60)	**8** (8), **9** (4), **10** (73)
3	1:6.2	*hv*, (60)	**8** (38), **9** (35), **10** (15)
4[e]	1:1.1	*hv*, (60)	**8** (34), **9** (29),[f] **10** (—)

[a] The concentration of substrate was 6.66×10^{-3} M. The concentration of nucleophile was 1.4×10^{-2} M, unless otherwise indicated.
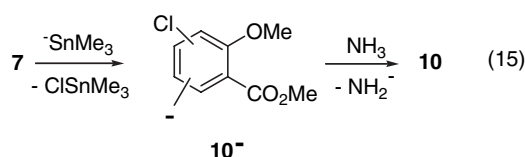[b] Quantified by GLC by the internal standard method with *p*-dibromobenzene as reference.
[c] The concentration of nucleophile was 2.1×10^{-2} M.
[d] Relative yields. Substrate recovered in 14%.
[e] The concentration of nucleophile was 6.66×10^{-3} M.
[f] Together with hydrolyzed compound.

$$7 \xrightarrow[\text{- ClSnMe}_3]{\text{}^-\text{SnMe}_3} \boxed{\begin{array}{c} \text{Cl} \quad \text{OMe} \\ \\ \text{CO}_2\text{Me} \end{array}}^- \xrightarrow[\text{- NH}_2^-]{\text{NH}_3} \mathbf{10} \qquad (15)$$

10$^-$

In addition to this, the photostimulated reaction of **7** in excess with $^-$SnMe$_3$ ions rendered the disubstitution **8** and monochloro substitution product **9** in 34% and 29% yields, respectively. The reduced product **10** was not formed in this experimental condition (Table 2, experiment 4).

Reactions of Atrazine (11) with $^-$SnMe$_3$ ions in liquid ammonia

2-chloro-N^4-ethyl-N^6-isopropyl-1,3,5-triazin-4,6-diamine (**11**) (Atrazine) is an herbicide used as a selective herbicide on corn and by control broadleaf and grassy weeds. It is effectively non-toxic to birds but readily the gastrointestinal tract. It is slightly toxic to fish and other aquatic life, though low bioaccumulation. It can be absorbed orally, dermal, and by inhalation and it is slightly to moderately toxic to humans and other animals. It has potential for groundwater contamination.

Substrate **11** is quite insoluble in liquid ammonia, and no reaction occurs under irradiation with $^-$SnMe$_3$ ions. In order to improve the solubility, **11** was added with a small amount of DMSO. In this experimental condition, **11** reacts under photostimulation with $^-$SnMe$_3$ ions to give the reduction and substitution products **12** and **13** in 26% and 40% yields, respectively [Eqn (16)]. This reaction did not occur neither without a little volume of DMSO nor in the dark conditions. The photostimulated reaction was inhibited by *p*-DNB (Table 3, experiments 1–5).

(16)
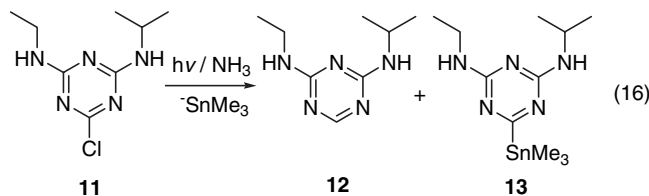
Table 3. Reaction of Atrazine (**11**) with $^-$SnMe$_3$ ions in liquid ammonia[a]

Experiment	11 : $^-$SnMe$_3$ ratio	DMSO (mL)	Conditions (min)	Products (%)[b]
1	1:1.1	—	*hv*, (150)	**12** (—), **13** (—)
2	1:1.1	6	*hv*, (150)	**12** (26), **13** (40)
3	1:1.1	4	*hv*, (210)	**12** (14), **13** (39)
4	1:1.1	4	Dark (210)	**12** (—), **13** (—)
5[c]	1:1.1	4	*hv*, (210)	**12** (—), **13** (—)
6[d]	1:3.2	6	*hv*, (150)	**12** (56), **13** (—)
7[d]	1:3.2	1	*hv*, (150)	**12** (43), **13** (—)
8[d]	1:3.2	1	Dark (150)	**12** (—), **13** (—)

[a] The concentration of substrate and nucleophile were 3.33×10^{-3} M, unless otherwise indicated.
[b] Relative yields. Substrate recovered in all reactions.
[c] *p*-DNB (20 mol%) was added.
[d] The concentration of substrate was 3.33×10^{-3} M. The concentration of nucleophile was 1.0×10^{-2} M.

The photostimulated reaction was performed in the presence of an excess of nucleophile in order to obtain the best conditions by the coupling reaction; however, reduced product **12** was obtained exclusively. The fact that the higher concentration of nucleophile affords **12** and that the reaction was inhibited by *p*-DNB suggest that reaction proceeds by a radical process but the coupling reaction is not efficient. Atrazine reacts by a reduction reaction faster than by the S$_{RN}$1 mechanism when an excess of nucleophile was used (Table 3, experiments 6–8).

Finally, the fact that photostimulated reactions of **11** with $^-$SnMe$_3$ afforded the reduction and substitution products, and this reaction did not occur in the dark, and both reactions were inhibited by *p*-DNB is indicative that **11** reacts with this anion by an ET process (Scheme 3). When **11** receives an electron it forms its radical anions, which fragment to afford radical **14** [Eqn (17)]. This radical intermediate has two competing processes: coupling with $^-$SnMe$_3$ ions to afford the substitution product **13** [Eqn (18)], or being reduced to product **12** [Eqn (19)].

The fact that the main product is the reduction product **12** is indicative that the coupling reaction of the radical
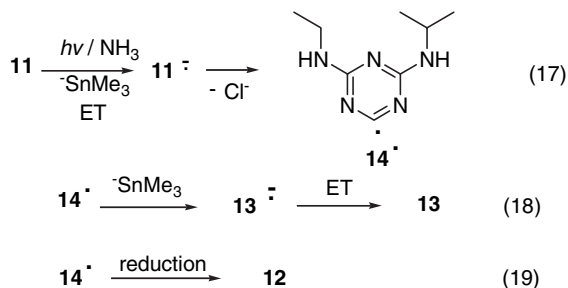
Scheme 3
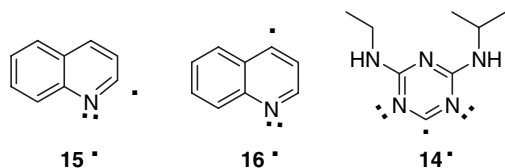
Scheme 4

14 with the anion is not efficient, probably due to electronic reasons, and the radicals are reduced to **12**.

It has been determined that the coupling rate of 2-quinolyl radical (**15**·) with $^-$OP(EtO)$_2$ and $^-$CH$_2$COMe ions (2.6×10^7 and $1.0 \times 10^7 \, \text{M}^{-1} \text{s}^{-1}$, respectively) are substantial lower than the coupling rate of 4-quinolyl radicals (**16**·) with the same nucleophiles (1.6×10^9 and $5.4 \times 10^9 \, \text{M}^{-1} \text{s}^{-1}$, respectively). These observations were rationalized by the existence of an electronic repulsion between the lone pair electrons on the nitrogen and the electrons of the Nu$^-$.[14] This repulsion contributes to decrease the coupling rate (Scheme 4). Radical **14**· has two lone pairs which decrease the coupling rate with the nucleophile even more.

CONCLUSIONS

Aryltrimethyl stannanes are valuable intermediates in organic syntheses, and the fact that they can be easily synthesized through the $S_{RN}1$ mechanism opens up important synthetic routes, such as stannanes intermediates in cross coupling reaction with different electrophiles catalyzed by palladium. These $S_{RN}1$ reactions are compatible with many functional groups compared to the drastic experimental conditions of other trimethylstannylation reactions.

We have reported the conversion of different substrates to aryltrimethylstannanes by reaction with $^-$SnMe$_3$ ions under irradiation. Thus, disubstituted methyl 2,5-bis(trimethylstannyl)benzoate (**2**, 99%), methyl 2-methoxy-3,6-bis(trimethylstannyl)benzoate (**8**, 64%), and substituted N^2-ethyl-N^4-isopropyl-6-trimethylstannyl-1,3,5-triazin-2,4-diamine (**13**, 40%) were obtained. These

results can be of great interest to obtain these compounds as precursors in organic synthesis.

EXPERIMENTAL

Methods

Irradiation was conducted in a reactor equipped with two 400-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water-refrigerated). The HRMS were recorded at UCR Mass Spectrometry Facility, University of California, United States.

Materials

Methyl 2,5-dichlorobenzoate, Dicamba, Atrazine, trimethylstannyl chloride and potassium t-butoxide (KOtBu) were commercially available and used as received. DMSO was distilled under vacuum and stored under molecular sieves (4 Å). Liquid ammonia was distilled under nitrogen and Na metal, and used immediately.

Preparation of methyl 3,6-dichloro-2-methoxybenzoate (7)

The 3,6-dichloro-2-methoxybenzoic acid (1 g, 4.5 mmol) was added to 0.5 g., 4.5 mmol of KOtBu dissolved in 25 mL of dry DMSO. Then, the reaction was quenched with a 0.8 mL, 12.5 mmol of methyliodide. The solution was dissolved with water and then extracted with diethyl ether. The product was isolated as yellow oil and identified by GC/MS. Identified by comparison with NIST Mass Spec Data of bibliography.[15]

Photostimulated reactions of 1 and 7 with $^-$SnMe$_3$ ions in liquid ammonia

The following procedure is representative of these reactions. Me$_3$SnCl (2.2 mmol or 3.2 mmol, respectively) and then Na metal (5.3 mmol or 7.7 mmol respectively, 20% excess) in small pieces were added to 150 mL of distilled ammonia, until total decoloration between two consecutive additions, and 20 min after the last addition, when no more solid was present, $^-$SnMe$_3$ ions were ready for use (lemon yellow solution). The substrate **1** or **7** (1 mmol) was added to the solution, and the reaction mixture was irradiated. Then, the reaction was quenched with an excess of ammonium nitrate, and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with diethyl ether. The products were isolated by column chromatography. In the other

experiments the products were quantified by GLC using the internal standard method.

Photostimulated reactions of 11 with $^-$SnMe$_3$ ions in liquid ammonia

The procedure was similar to that for the previous reaction, except from the fact that Me$_3$SnCl (1.2 mmol) and then Na metal (2.6 mmol, 20% excess) in small pieces was added to 300 mL of distilled ammonia. Next, the substrate 11 (1 mmol) dissolved in dry DMSO was added to the solution and them the reaction mixture was irradiated.

Reactions of 1, 7, and 11 with $^-$SnMe$_3$ ions in liquid ammonia in the dark

The procedure was similar to that for the previous reaction, except that the reaction flask was wrapped with aluminum foil.

Inhibited reactions with $^-$SnMe$_3$ ions in liquid ammonia

The procedure was similar to that for the previous reaction, except that 20 mol% of *p*-DNB or di-*ter*-butyl nitroxide was added to the solution of nucleophile prior to substrate addition.

Isolation and identification of products

Methyl 2,5-*Bis-trimethylstannanylbenzoate (2): Isolated as a white solid after column chromatography on silica gel, eluted with pentane. Mp: 113–113.7 °C. ^{1}**H-NMR** (CDCl$_3$) δ: 0.25 (9H, s, $J_{H–Sn} = 27$ Hz); 0,31 (9H, s, $J_{H–Sn} = 27$ Hz); 3.92 (3H, s); 7,64 (2H, s); 8,23 (1H, s). ^{13}**C-NMR** (CDCl$_3$) δ: −9.57; −7.51; 52.23; 134.54; 136.00; 136.97; 139.31; 142.55; 146.68; 169.21. **EM** (EI+) *m/z* (%): 449 (80), 447 (100), 417 (22), 400 (6), 284 (5), 216 (35), 201 (23), 135 (9), 133 (6). HRMS (CI) exact mass calcd for C$_{14}$H$_{24}$O$_2$Sn$_2$ 463.9820 found 463.9811.[16]

Methyl 2-chloro-5-trimethylstannanylbenzoate and methyl 5-chloro-2-trimethylstannanyl benzoate (3): Isolated as yellow oil after Kügelrohr distillation (50 °C/1 mm Hg). ^{1}**H-NMR** (CDCl$_3$) δ: 0.27 (9H, s, $J_{H–Sn} = 27$ Hz); 3.92 (3H, s); 7.49–7.61 (2H, m); 8.08–8.09 (1H, d). ^{13}**C-NMR** (CDCl$_3$) δ: −9.57; −7.38; 52.57; 129.81; 131.79; 137.68; 167.82. **EM** (EI+) *m/z* (%): 319 (100), 317 (73), 302 (4), 289 (50), 287 (36), 272 (3), 261(6), 259 (14), 231 (5), 165 (2), 151 (24), 133 (7), 118 (5), 89 (5), 75 (7), 63 (4). HRMS (CI) exact mass calcd for C$_{11}$H$_{15}$ClO$_2$Sn (—CH$_3$) 318.9548, found (M$^+$— CH$_3$) 318.9553.[17]

Methyl 2-methoxy-3,6-bis-trimethylstannanylbenzoate (8): Isolated as a white solid after column chromatography on silica gel, eluted with pentane. Mp: 62.5–63.5 °C. ^{1}**H-NMR** (CDCl$_3$) δ: 0.27 (9H, s, $J_{H–Sn} = 54.2$ Hz); 0.33 (9H, s, $J_{H–Sn} = 55.2$); 3,77 (3H, s); 3.93 (3H, s); 7.33–7.36 (1H, d, $J_{H–Sn} = 6.8$ Hz); 7.51–7.54 (1H, d, $J_{H–Sn} = 6.8$).^{13}**C-NMR** (CDCl$_3$) δ: −8.64; −7.60; 52.33; 62.71; 129.12; 131.37; 137.08; 139.30; 148.38; 164.59; 169.98. **EM** (EI+) *m/z* (%): 479 (76), 477 (100), 475 (94), 445 (19), 430 (3), 415 (19), 385 (7); 230 (17), 214 (11), 165 (6), 151 (7). HRMS (CI) exact mass calcd for C$_{15}$H$_{26}$O$_3$Sn$_2$ (—CH$_3$) 478.9691, found (M$^+$—CH$_3$) 478.9695.[17]

N^2-ethyl-N^4-isopropyl-6-trimethylstannanyl-1,3,5-triazin-2,4-diamine (13): White solid that decomposed in column chromatography on silica gel. ^{1}**H-NMR** (CDCl$_3$) δ: 0.27 (9H, s, $J_{H–Sn} = 27.6$ Hz); 1.13–1.21 (9H, m); 3.37–3.39 (2H, m); 4.08–4.16 (1H, m). ^{13}**C-NMR** (CDCl$_3$) δ: −9.53; −2.47; 14.82; 22.71; 35.25; 42.02; 162.41; 162.98; 165.28. **EM** (EI+) *m/z* (%): 334(6), 330(37), 328(27), 298(1), 260(3), 237(19), 233 (18); 219 (15), 203 (3), 180 (100), 163 (7). HRMS (EI) exact mass calcd for C$_{11}$H$_{23}$N$_5$Sn$_2$ 345.0975, found (MH$^+$) 346.1062.

N^2-Ethyl-N^4-isopropyl-1,3,5-triazin-2,4-diamine (12): Isolated as a white solid after column chromatography on silica gel, eluted with pentane/ethyl ether (80:20). Mp: 181–182 °C. ^{1}**H-NMR** (CDCl$_3$) δ: 1.17–1.22 (9H, m); 3.37–3.44 (2H, m); 4.13–4.16 (1H, m); 7.99 (1H, s). ^{13}**C-NMR** (CDCl$_3$) δ: 13.77; 22.72; 35.44; 42.28; 165.16; 172.26. **EM** (EI+) *m/z* (%): 181(86), 166(94), 153(4), 138(34), 136(3), 124(18), 122 (29); 111 (25), 98(17), 96 (17), 83 (19), 71(67), 58(100), 55(21). HRMS (EI) exact mass calcd for C$_8$H$_{15}$N$_5$ 181.1327, found 181.1324.

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13. It has been demonstrated before that when the HME is faster than the $S_{RN}1$ mechanism the anion formed is protonated very fast by liquid ammonia, see Ref. 2.

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16. All new compounds were purified by column chromatography and were determined to be >95% pure by GLC and NMR.

17. We have tried DEI, CI, FAB, and even laser desorption and we always see the loss of a methyl group.