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Synthesis of Arylstannanes from Arylamines

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*Summary: Arylamines have been converted into aryltrimethylammonium salts, which on reaction with sodium trimethylstannide (**1**) in liquid ammonia afford aryltrimethylstannanes by the $S_{RN}1$ mechanism. With (4-methoxyphenyl)- (**2**), (1-naphthyl)- (**4**), phenyl- (**6**), (4-acetylphenyl)- (**8**), and (4-cyanophenyl)trimethylammonium salts (**10**) the substitution products are obtained in good to excellent yields (45−100%). Also, the photostimulated reaction of (2-pyridyl)trimethylammonium iodide (**12**) with **1** leads to the substitution product **13** (50%). With (4-chlorophenyl)trimethylammonium iodide (**14**) the disubstitution product **19** is obtained in 76% yield. On the other hand, the results obtained in the reaction of (4-bromophenyl)trimethylammonium iodide (**15**) with **1** clearly indicate a fast HME reaction in the dark. The ET process ($S_{RN}1$) competes, although inefficiently, under irradiation.*

Introduction

The $S_{RN}1$ (unimolecular radical nucleophilic substitution) is a well-known process.[1] The proposed mechanism is a chain process.

Triorganostannyl anions have proved to be excellent nucleophiles in $S_{RN}1$ reactions.[2] We have recently described the photostimulated reactions of haloarenes and haloheteroarenes with triphenylstannyl anions in dimethyl sulfoxide[3] and the photostimulated reactions of aryldiethyl phosphate esters with trimethyl- and triphenylstannyl anions in liquid ammonia.[4] All these substrates, under the reaction conditions studied, gave substitution products in good to excellent yields. The main advantage of these reactions is that they enable the direct synthesis of organostannanes with different aryl ligands,[1] avoiding the use of organomagnesium or organolithium reagents.

A great variety of aromatic compounds with appropriate leaving groups have been shown to react by the $S_{RN}1$ mechanism. Various leaving groups, including Me_3N^+, have been used.[1] We report here the results obtained in the reactions of a number of aryltrimethylammonium salts with trimethylstannylsodium (**1**) in liquid ammonia. These reactions are of interest not only from a mechanistic point of view but also as a suitable synthetic route to arylstannanes. As far as we know, there are no reports in the literature concerning the reaction between triorganotin anions and aryltrimethylammonium salts. The increasing importance of aryltrialkylstannanes in recent years is connected with their use as substrates in palladium-catalyzed reactions.[5]

Table 1. Reaction of Aryl- and Heteroaryltrimethyl Ammonium Salts with Me_3SnNa in Liquid NH_3[a]

entry	aryl moiety[b]	conditions; time (h)	$(Ar)SnMe_3$ or 1,4-$(Me_3Sn)_2C_6H_4$, yield (%)[c]
1	4-An	dark; 0.5	$(4\text{-An})SnMe_3$, 14
2	4-An	*hν*; 0.5	$(4\text{-An})SnMe_3$, 100
3	4-An	dark; 0.5[d]	0
4	4-An	*hν*; 0.5[d]	$(4\text{-An})SnMe_3$, 34
5	1-naph	*hν*; 5	$(1\text{-Naph})SnMe_3$, 85
6	1-naph	dark; 5	0
7	Ph	*hν*; 4	$(Ph)SnMe_3$, 89
8	Ph	dark; 4	0
9	4-AcPh	*hν*; 6	$(4\text{-AcPh})SnMe_3$, 45
10	4-AcPh	dark; 6	0
11	4-CNPh	*hν*; 0.08	$(4\text{-CNPh})SnMe_3$, 100
12	4-CNPh	dark; 0.08	$(4\text{-CNPh})SnMe_3$, 100
13	4-CNPh	dark; 0.08[d]	$(4\text{-CNPh})SnMe_3$, 35
14	2-Pyr	*hν*;4	$(2\text{-Pyr})SnMe_3$, 50
15	2-Pyr	dark; 4	0
16	4-ClPh[e]	*hν*; 5	1,4-$(Me_3Sn)_2C_6H_4$, 76
17	4-ClPh[e]	dark; 5	1,4-$(Me_3Sn)_2C_6H_4$, 12
18	4-ClPh[e]	*hν*; 5[d]	1,4-$(Me_3Sn)_2C_6H_4$, 18
19	4-ClPh[e]	dark; 5[d]	0
20	4-BrPh[e]	*hν*; 5	1,4-$(Me_3Sn)_2C_6H_4$,6[f]
21	4-BrPh[e]	dark; 5	0

[a] Substrate/Me_3SnNa, 1/1.2. [b] Abbreviations: 4-Anisyl, 4-An; 1-naphthyl, 1-Naph; phenyl, Ph; 4-acetylphenyl, 4-AcPh; 4-cyanophenyl, 4-CNPh; 2-pyridyl, 2-pyr; 4-chlorophenyl, 4-ClPh; 4-bromophenyl, 4-BrPh. [c] Determined by GC. [d] 20% *p*-DNB added. [e] Substrate/Me_3SnNa, 1/2.2. [f] Together with $Me_3SnC_6H_5$, 55%.

Results and Discussion

We have found that there is a slow reaction of (4-methoxyphenyl)trimethylammonium iodide (**2**) with **1** in the dark, giving the substitution product (4-methoxyphenyl)trimethylstannane (**3**) in 14% yield (30 min). On the other hand, when the reaction is carried out under irradiation, **3** is obtained in quantitative yield (30 min) (Table 1, entries 1 and 2). Both reactions are totally or partially inhibited by the addition of *p*-dinitrobenzene (*p*-DNB) (20%), a well-known inhibitor of $S_{RN}1$ reactions[1] (entries 3 and 4).

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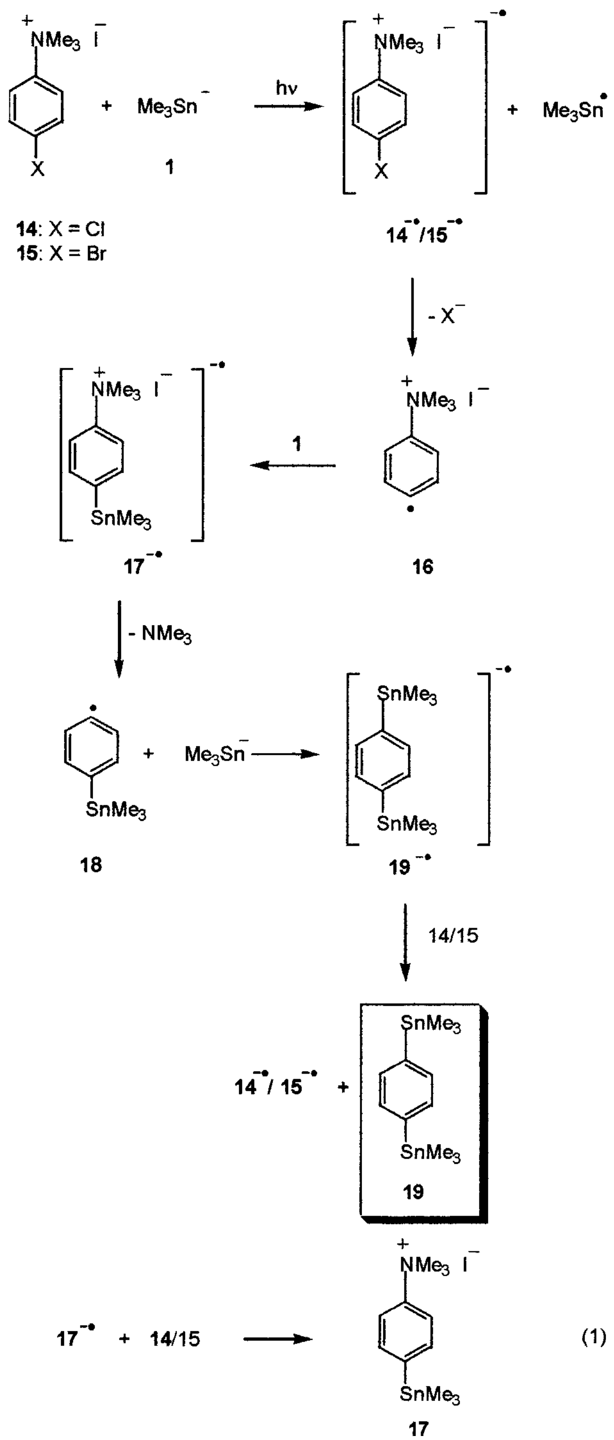
Scheme 1

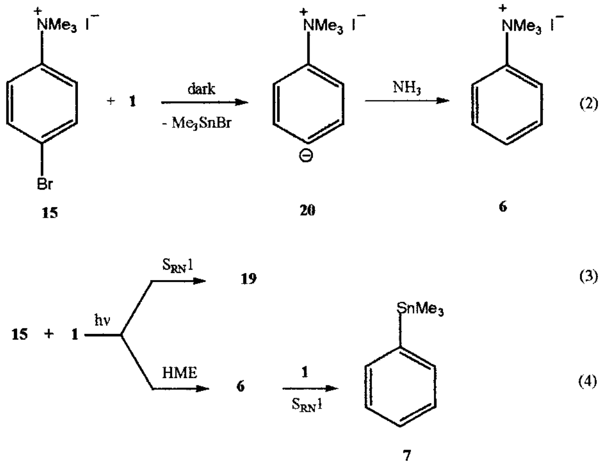


Moreover, the photostimulated reactions of (1-naphthyl)trimethylammonium iodide (**4**) and phenyltrimethylammonium iodide (**6**) with **1** yield the substitution products (1-naphthyl)trimethylstannane (**5**) in 85% yield (5 h) and phenyltrimethylstannane (**7**) in 89% yield (4 h), respectively (entries 5 and 7). It should be noted that with both substrates no reaction occurred in the dark (entries 6 and 8). Similar results were obtained from ammonium salts, supporting different substituents on the aryl moiety. Also, (4-acetylphenyl)trimethylammonium iodide (**8**) reacts with **1**, leading after 6 h under irradiation to (4-acetylphenyl)trimethylstannane (**9**) in 45% yield; there is no reaction between **8** and **1** in the dark (entries 9 and 10). On the other hand, the reaction of (4-cyanophenyl)trimethylammonium sulfate (**10**) with **1**, either under irradiation or in the dark, led (5 min) to quantitative yields of (4-cyanophenyl)trimethylstannane (**11**) (entries 11 and 12). It should be noted that the spontaneous reaction in the dark was partially inhibited by the addition of *p*-DNB (entry 13). It can also be observed in Table 1 that (2-pyridyl)trimethylammonium iodide (**12**) did not react with **1** in the dark (4 h), but under irradiation the corresponding substitution product 2-(trimethylstannyl)pyridine (**13**) was formed in good yield (4 h, 50%) (entries 14 and 15). All of these results suggest that the reactions of **2**, **4**, **6**, **8**, **10**, and **12** with **1** take place by the $S_{RN}1$ mechanism.

We have found that also substrates containing two leaving groups react with **1** under irradiation. Thus, (*p*-chlorophenyl)trimethylammonium iodide (**14**) led after 5 h under irradiation to 1,4-bis(trimethylstannyl)benzene (**19**) (76%). There is a spontaneous reaction of **14** with **1** in the dark, giving disubstitution product **19** in 12% yield. It should be noted that no monosubstitution product was detected and that the reaction was partially or completely inhibited in the presence of *p*-DNB (entries 16–19). These results clearly indicate that this disubstituted substrate also reacts with **1** by the $S_{RN}1$ mechanism, as shown in Scheme 1.

The fact that in this reaction the monosubstitution product was not detected suggests that the fragmentation reaction of $\mathbf{17}^{\bullet-}$ to give **18** is faster than the electron transfer (ET) to **14** (Scheme 1, eq 1).

On the other hand, the photostimulated reaction of (*p*-bromophenyl)trimethylammonium iodide (**15**) with **1** led (5 h) to a mixture of disubstitution product **19** (6%) and phenyltrimethylstannane (**7**) in 55% yield (entry 20). The reaction carried out in the dark gave (5 h) a mixture of phenyltrimethylammonium salts, and no substitution product was detected (entry 21). These results clearly indicate a fast halogen–metal exchange (HME) reaction in the dark followed by the protonation of the intermediate anion **20** by the ammonia to give **6** (eq 2). The ET process ($S_{RN}1$) competes, although inefficiently, under irradiation. Meanwhile, through an $S_{RN}1$ mechanism product **19** is formed, as shown in Scheme 1, the HME mechanism gives **6** as intermediate, which reacts with **1**, leading to **7** through an $S_{RN}1$ mechanism (eq 4). It should be noted that without adding water during the workup it was possible to



isolate trimethyltin iodide as product, probably formed by an halogen exchange reaction between trimethyltin bromide and iodide anion.

The obtained results demonstrate that the conversion of arylamines into the corresponding aryltrimethylammonium salts followed by the $S_{RN}1$ displacement with trimethyltin anions in liquid ammonia is an excellent and convenient method for the synthesis of arylstannanes. This method has the advantage that various substituents in the aromatic ring are tolerated. Further work is in progress to study the scope of the reaction.

Experimental Section

General Procedures. Irradiation was conducted in a water-cooled reactor made of Pyrex, equipped with four 250 W UV lamps emitting maximally at 350 nm. Most of the reagents were available commercially. Ammonium salts were prepared by known procedures.[6] All the products obtained were characterized by comparison of their physical, MS, and NMR spectroscopic characteristics with those of an authentic sample prepared by known procedures.[2−4] They were quantified by GC using the external standard method. The reaction flask was wrapped with aluminum foil to carry out the reactions in the dark.

Photostimulated Reaction of (4-Methoxyphenyl)trimethylammonium Iodide (2) with Me_3SnNa. The reactions were performed by following the same procedure in all cases. A 150 mL amount of sodium-dried ammonia was condensed into a 250 mL three-necked, round-bottomed Pyrex flask equipped with a cold finger condenser, a nitrogen inlet, and a magnetic stirrer. Me_3SnCl (0.219 g, 1.1 mmol) and Na metal (0.058 g, 2.53 mmol) were added. When the blue color disappeared, **2** (0.293 g, 1.00 mmol) was added and then the mixture was irradiated with stirring for 30 min. The reaction was quenched by adding MeI in excess, and ammonia was allowed to evaporate. The residue was treated with water and then extracted with ether. The products were quantified by GLC by the external standard method (100%), compared with an authentic sample synthesized by a known procedure.[4]

Photostimulated Reaction of 2 with Me_3SnNa in the Presence of *p*-DNB. The procedure was similar to that for the previous reaction, but with the addition of *p*-DNB (20 mol %) to the solution of the nucleophile before substrate addition.

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