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Reaction of trimethyltin 1-pentanethiolate with *N*-chloro-*N*-sodium-4-chlorobenzenesulfonamide

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The reaction of trimethyltin 1-pentanethiolate with *N*-chloro-*N*-sodium-4-chlorobenzenesulfonamide proceeds in anhydrous methanol *via* the initial cleavage of the tin—sulfur bond (desulfurization process) and subsequent imination of the sulfenylamide group of *N*-trimethylstannyl-*N*-(1-pentyl)sulfenyl-4-chlorobenzenesulfonamide with a second molecule of the chloroamide.

Key words: trimethyltin 1-pentanethiolate; monochloroamine; desulfurization; oxidative imination.

The reaction of organic sulfides R_2S with sodium monochloramides of arensulfonic acids $Na(Cl)NSO_2Ar$ is well studied.[1] It results in the formation of sulfonylsulfimides (sulfonylsulfylimines) $R_2S{=}NSO_2Ar$ (oxidative imination). Organometallic analogs, *e. g.*, trialkyltin sulfides $(R_3Sn)_2S$, have more polar metal—sulfur bonds than carbon—sulfur bonds. For this reason, the previously studied reaction[2] of trimethyltin sulfide with *N*-sodium-*N*-chloramine (CA) occurs with the cleavage of both of the tin—sulfur bonds and liberation of elemental sulfur (oxidative desulfurization).

In trialkyltin thiolates R_3SnSR sulfur is simultaneously bound with carbon and tin. Hence, the liberation of elemental sulfur in the interaction with CA is impossible due to the strong bond of the sulfide sulfur with carbon, and the imination of the sulfur atom to form organotin sulfylimine $Me_3SnS({=}NSO_2Ar)Am$ (**1**) is unlikely due to the primary cleavage of the tin—sulfur bond (desulfurization).

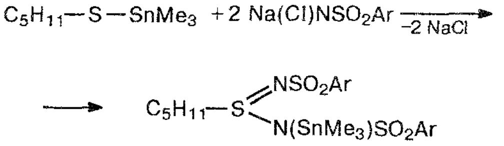
The reaction of CA with trimethyltin 1-pentanethiolate Me_3SnSAm was studied in anhydrous methanol to continue the studies of the reactive capabilities of the system CA—organotin halogen- or sulfur-containing compounds.[2–4]

Results and Discussion

As in the case of oxidation of mercaptans with sodium monochloramines,[5] or of sodium arylmercaptides with *N*,*N*-dichloramides of arensulfonic acids,[6] the formation of diamyldisulfide can be expected for the interaction of trimethyltin 1-pentanethiolate with CA. However, only minor amounts of diamyldisulfide (5—6 %) were found in the reaction products by chromatography, while the overall conversion of initial reagents was 87 %. A double amount of CA is needed for the complete reaction of the organotin compound. A colorless, amorphous, and very hygroscopic organotin compound was the main reaction product. Its IR spectrum contains the absorption band with a maximum at 940 cm^{-1} assigned[1,7,8] to the stretching vibrations of the S=N bond, which attests to the formation of the product of sulfur imination. Characteristic bands of the aromatic ring, SO_2-, and Me_3Sn-group are also observed. There is a considerable loss of tin after recrystallization of the substance from water due to hydrolysis of the Sn—N bond. Therefore, in all cases one should work with anhydrous solvents either in a dry atmosphere or *in vacuo.*

Taking into account the ratio of reagents, the data of IR spectroscopy, which confirm the process of oxidative imination of the sulfide sulfur, and the results of elemental analysis, we suggest a general equation for the reaction studied (Scheme 1).

Scheme 1



2

Ar = 4-Cl—C_6H_4

We define product **2** as the amide derivative of pentaiminosulfinic acid $C_5H_{11}S({=}NH)OH$: *N*-(trimethylstannyl)-4-chlorobenzenesulfonylamide of *N'*-(4-chlorobenzenesulfonyl)pentaiminosulfinic acid. Similar

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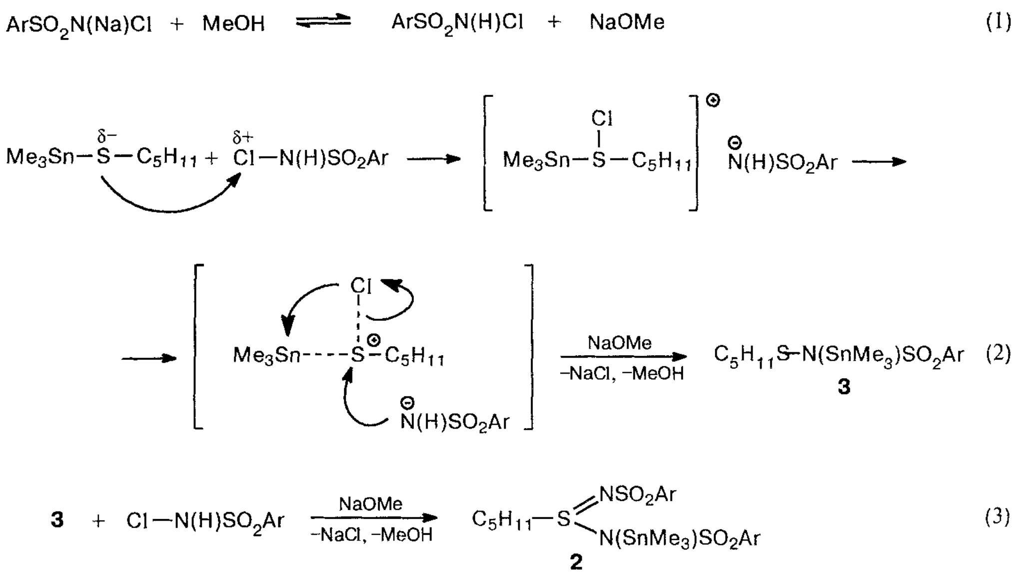
Scheme 2



sodium salts[9] $RS(=NSO_2Ar)N(Na)SO_2Ar'$ are named as salts of *N,N'*-bis(arylsulfonyl)alkanesulfinamidines. However, they were not isolated in individual state and were identified by the precipitation of the corresponding amidines $RS(=NSO_2Ar)N(H)SO_2Ar'$ on acidification of the solutions. Amidines of this general formula have been known since 1930.[5,10]

We believe that the overall reaction (Scheme 1) involves several stages, beginning from solvolysis of the initial CA in methanol (Scheme 2).

As in the case of trimethyltin sulfide,[2] there is a nucleophilic interaction of the sulfide sulfur atom, which carries a partial negative charge, with a positively charged center in CA.[1] The subsequent course of the reaction is determined by the transformation of the intermediate formed (Scheme 2, reaction 2).

The ratio of the reagents at stage (2) is 1 : 1. Sulfenamide **3** formed is isomeric to compound **1** and is not accumulated in the reaction mixture, undergoing imination at two-valence sulfur with the second molecule of CA to give the final product **2** (Scheme 2, reaction 3).

Non-organometallic iminated products of type **2**, $RS(=NSO_2Ar)N(X)SO_2Ar$, are known and can be obtained, *e. g.*, as by-products in oxidation of thiols (X = H) with chloramine-T[1,11] or as the main product in oxidation of sodium thiolates (X = Na) with *N,N*-dichloramide of arensulfonic acids.[9,12]

Compound **2** is almost unchanged after a short period in moist air; however, it quantitatively hydrolyzes in a weakly acidic alcohol medium at the tin—nitrogen bond to give 4-chlorobenzenesulfonylamide of (4-chlorobenzenesulfonyl)pentaniminosulfinic acid $C_5H_{11}S(=NSO_2C_6H_4Cl\text{-}4)N(H)SO_2C_6H_4Cl\text{-}4$ (**4**).

Experimental

Purification of CA and determination of active chlorine were performed according to the procedure described in Ref. 3.

IR spectra were recorded on a Perkin-Elmer 577 instrument (a thin film in Vaseline oil, KBr).

Anhydrous methanol was prepared prior to use by refluxing with magnesium methylate with subsequent distillation in a dry atmosphere.

Sulfur in the presence of halogen was quantitatively determined by combustion according to Schoenherr.

Synthesis of trimethyltin 1-pentanethiolate and dimethyltin di-1-pentanethiolate. The mixture of 7.82 g (43 mmol) of trimethyltin hydroxide and 4.51 g (43 mmol) of 1-pentanethiol in 100 mL of toluene was refluxed for several minutes, the azeotropic mixture with the main portion of the solvent was distilled off, and the rest of the solvent was completely removed under reduced pressure. After distillation *in vacuo* of non-volatile liquid, 8.50 g (32 mmol) of trimethyltin 1-pentanethiolate was obtained (74 %), b. p. 41—42 °C (0.5 Torr). Found (%): C, 36.07; H, 7.75; S, 11.03; Sn, 44.46. $C_8H_{20}SSn$. Calculated (%): C, 35.99; H, 7.54; S, 12.01; Sn, 44.46.

A solution of 6.73 g (53 mmol) of sodium 1-pentanethiolate in 100 mL of methanol was added dropwise with stirring to a solution of 5.87 g (26 mmol) of dimethyltin dichloride in 50 mL of ether. The reaction mixture was refluxed for 2 h, the precipitated NaCl was filtered off, and the filtrate was evaporated *in vacuo*. Ether (100 mL) was added to the non-volatile liquid residue, and an additional amount of NaCl was filtered off. The filtrate was evaporated *in vacuo* to give after distillation 6.12 g (17 mmol) of dimethyltin di-1-pentanethiolate (65 %). B. p. 143—144 °C (1.5 Torr). Found (%): C, 40.58; H, 8.64; S, 17.03; Sn, 33.00. $C_{12}H_{20}S_2Sn$. Calculated (%): C, 40.58; H, 7.94; S, 18.05; Sn, 33.42.

Reaction of trimethyltin 1-pentanethiolate with sodium monochloramide of 4-chlorobenzenesulfonic acid. Small portions of a solution of 3.13 g (11.7 mmol) of trimethyltin 1-pentanethiolate in 10 mL of methanol was added *in vacuo* to a solution of 3.06 g (11.7 mmol) of CA in 20 mL of methanol at 0 °C. The reaction mixture was kept at ~20 °C for 1 day, and then the solvent was completely removed at reduced pressure to a trap cooled with liquid nitrogen. The non-volatile residue was treated with 30 mL of anhydrous CH_2Cl_2, the precipitated NaCl (0.59 g, 86 %) was filtered off, and the filtrate was evaporated at reduced pressure to a trap cooled with liquid nitrogen. A viscous residue (6.5 g) was extracted with anhydrous hexane (2×30 mL) and the liquid was decanted from the solidified mass. After drying *in vacuo* 3.68 g (5.69 mmol) of product **2** was obtained in the form of a colorless amorphous substance. The substance melts in the range of 65—70 °C (evacuated capillary). Found (%): C, 37.45; H, 4.32; S, 14.58; Sn, 17.38. $C_{20}H_{28}Cl_2N_2O_4S_3Sn$. Calculated (%): C, 37.17; H, 4.37; S, 14.78; Sn, 18.37. IR spectrum (ν/cm^{-1}): 1260 (as, SO_2); 1145, 1080 (s, SO_2); 940 (S=N); 775 (δ Sn—Me); 570 (Sn—C). The hexane extract was evaporated at reduced pressure to a trap cooled with liquid nitrogen. In the oily non-volatile residue (0.64 g), the total amount of the unreacted trimethyltin 1-pentanethiolate and trimethyltin methoxide was determined by acid titration with Congo red (1.94 mg-eq). Then the content of trimethyltin 1-pentanethiolate was determined by iodometry (1.47 mg-eq; 0.39 g). The content of trimethyltin methoxide in this residue was calculated from the difference between the acid and iodometric titrations, which was 0.47 mg-eq (0.085 g). Diamyldisulfide (0.15 g, 0.7 mmol) was also found by chromatography. The contents of trimethyltin 1-pentanethiolate (2.09 mmol) and trimethyltin methoxide (0.6 mmoles) were determined in the solvents collected in traps first by acid and then by iodometric titrations of aliquots.

A solution of 1.32 g (2.0 mmol) of compound **2** in 25 mL of methanol was acidified with 0.1 *N* HCl to pH 4—3 (according to the indicator paper), and a colorless residue was filtered off to give 0.78 g (1.6 mmol) of hydrolysis product **4** with m.p. 154—156 °C (aqueous methanol). Found (%): C, 42.39; H, 4,16; S, 20.37. $C_{17}H_{20}Cl_2N_2O_4S_3$. Calculated (%): C, 42.23; H, 4.17; S, 19.90. IR spectrum (ν/cm^{-1}): 1340, 1310 (as, SO_2); 1170, 1145 (s, SO_2); 980 (S=N).

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