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XIII*. MOLECULAR ADDITION COMPLEXES OF TIN(IV) HALIDES WITH TETRAKIS(2-CYANOETHYL)TIN

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INTRODUCTION

Previous papers in this series[1] have dealt with the preparation of and the chemistry of a number of (2-cyanoethyl)tin derivatives. In the present paper, novel complexes of tin tetrachloride and bromide with tetrakis(2-cyanoethyl)tin are reported and discussed. At elevated temperatures, these complexes undergo redistribution reaction by themselves, with added tin(IV)halide ($X = Cl$ and Br), or with added tetrakis(2-cyanoethyl)tin, forming all three (2-cyanoethyl)tin halides as products.

DISCUSSION AND RESULTS

When either tin(IV)chloride or bromide is added to a solution of tetrakis(2-cyanoethyl)tin (I) in methylene chloride, a white solid immediately precipitates (eqn. 1). Elemental analysis and infrared spectroscopy have shown that these solids

$$(NCCH_2CH_2)_4Sn + SnX_4 \xrightarrow{CH_2Cl_2} (NCCH_2CH_2)_4Sn\cdot SnX_4 \quad X = Cl \text{ or } Br \quad (1)$$

are complexes which are composed of one mole of tetrakis(2-cyanoethyl)tin and one mole of tin(IV)halide. This complex is obtained, regardless of the stoichiometry used. If equimolar quantities of (I) and SnX_4 are employed, then the complexes (II) are obtained in virtually quantitative yield. Because of the sensitivity of these complexes to moisture, their preparation and isolation had to be carried out in an inert atmosphere. Under comparable experimental conditions, tin(IV)fluoride, iodide, sulfate, and oxide do not form complexes with compound (I).

TABLE 1

FREQUENCIES OF THE NITRILE ABSORPTION BANDS IN TETRAKIS(2-CYANOETHYL)TIN AND IN COMPLEXES WITH TIN TETRAHALIDES

Compound	*C≡N absorption frequency (cm^{-1})*
$(NCCH_2CH_2)_4Sn$	2242 (neat)
$(NCCH_2CH_2)_4Sn\cdot SnCl_4$	2268 (nujol mull)
$(NCCH_2CH_2)_4Sn\cdot SnBr_4$	2268 (nujol mull)

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* For Part XII see preceding paper[1b].

The nitrile stretching frequencies for $(NCCH_2CH_2)_4Sn$ and its complexes are summarized in Table 1. The change in frequency upon complex formation is 26 cm^{-1}, which is similar in magnitude and direction to that observed for complexes of tin tetrachloride with aliphatic[2] or aromatic[3] nitriles.

The increase in frequency is somewhat remarkable in that it requires a strengthening of the nitrile bonds upon complex formation. This seeming anomaly has recently been resolved by the work of Purcell and Drago[4]. Another remarkable aspect of this data is the occurrence of only one nitrile stretch, and only the higher stretching frequency at that, in the spectra of the complexes. We suggest this is due to the fact that the integrated intensities of adsorption for the complexed nitriles are at least ten times greater[3] than for the nitrile itself and the stretching vibrations of the uncomplexed nitriles are hidden by the more intense high frequency band.

The reaction of tin(IV)chloride (or bromide) with a tetraalkyl or tetraaryltin is known as the "redistribution reaction." Since the initial discovery of this reaction by Kocheshkov[5], it has been used extensively both in the laboratory and commercially as a method for preparing organotin halides[6].

When the complexes (II) are heated by themselves, with added SnX_4, or with added $Sn(CH_2CH_2CN)_4$, for several hours at 110–120°, a redistribution takes place yielding all three (2-cyanoethyl)tin halides. The products are obtained in moderate to poor yield with $(NCCH_2CH_2)_3SnX$ predominating, regardless of stoichiometry used. Table 2 summarizes the results that were obtained.

TABLE 2

SUMMARY OF REDISTRIBUTION REACTIONS ($R = -CH_2CH_2CN$)

Run	*Reactants molar ratio* $R_4Sn/SnBr_4$	*Reaction temp.* (°C)	*Reaction time* (h)	*Expected product*[a]	*Yields of products isolated* (%)			
					R_3SnBr[a]	R_2SnBr_2[b]	$RSnBr_3$	R_4Sn
1	3:1	[c]		R_3SnBr	31.3			
2	3:1	104	5	R_3SnBr	56.8			
3	3:1[d]	104	5	R_3SnCl	41.1			
4	1:1	120	4	R_2SnBr_2		7.7		
5	1:1	120	4	R_2SnBr_2		3.8		
6	1:1	104	5	R_2SnBr_2		< 1.0		
7	1:1	105	5	R_2SnBr_2	12.8[e]	5.9	4.3[e]	69.5[f]
8	1:3	104	5	$RSnBr_3$	50.0[e]	0	3.4	

[a] Isolated as the corresponding acetate, $R_3SnO_2CCH_3$. [b] Isolated as the corresponding sulfide, $(R_2SnS)_3$. [c] Reaction took off, reached a height of 147°, and then was rapidly cooled to room temperature. [d] $SnCl_4$ was used in place of $SnBr_4$. [e] Yield based on percent of $-CH_2CH_2CN$ groups in product over the total $-CH_2CH_2CN$ groups in reactants. [f] Recovered starting material.

A scheme to separate all three (2-cyanoethyl)tin bromides and unreacted tetrakis(2-cyanoethyl)tin from each other has been devised. It is based on the insolubility of mono(2-cyanoethyl)tin tribromide in hot CCl_4 and the solubility of tris(2-cyanoethyl)tin bromide and bis(2-cyanoethyl)tin dibromide in water. Tetrakis(2-cyanoethyl)tin (I) is insoluble in both solvents. Tris(2-cyanoethyl)tin bromide and bis(2-cyanoethyl)tin dibromide were identified by their conversion to the corresponding acetate and sulfide, respectively. The preparation and characterization of these derivatives was reported previously[1].

EXPERIMENTAL

All melting points were uncorrected and were determined using open capillary tubes in a Mel-Temp. Apparatus (Laboratory Devices, Cambridge, Mass.). Molecular weight determinations were carried out in a thermistor osmometer (Mechrolab Osmometer Model 301).

Infrared spectra were run on a Beckman IR-8 Infrared Spectrophotometer.

Tetrakis(2-cyanoethyl)tin. This compound was prepared according to the procedure described by Tomilov and Kaabak[7]. The product was purified by recrystallization from methylene chloride at −78°.

*Preparation of the tetrakis(2-cyanoethyl)tin/tin(IV) halide complexes**

1 : 1 *Tetrakis(2-cyanoethyl)tin/tin(IV) bromide complex.* To a solution of 16.7 g (0.05 mole) of tetrakis(2-cyanoethyl)tin in 25 ml of methylene chloride was added a solution of 21.9 g (0.05 mole) of tin(IV) bromide in 25 ml of methylene chloride. A white solid precipitated immediately and a slight rise in temperature was noticed. After the mixture had been stirred for an additional 30 min, the 1 : 1 tetrakis(2-cyanoethyl)tin/tin(IV) bromide complex which resulted was filtered, washed with methylene chloride, and dried in a vacuum dessicator for 2 h. A 98 % yield (37.8 g) was obtained, m.p. 119–121° (sealed capillary). (Found: Br, 40.80; N, 7.16; Sn, 30.82. $C_{12}H_{16}Br_4N_4Sn_2$ calcd.: Br, 41.35; N, 7.25; Sn, 30.71 %.)

1 : 1 *Tetrakis(2-cyanoethyl)tin/tin(IV) chloride complex.* The reaction of tetrakis(2-cyanoethyl)tin and tin(IV) chloride was carried out in the manner described above. From 3.35 g (0.01 mole) of tetrakis(2-cyanoethyl)tin and 2.61 g (0.01 mole) of $SnCl_4$, there was obtained 5.91 g (99 %) of the 1 : 1 $(NCCH_2CH_2)_4Sn \cdot SnCl_4$ complex, m.p. 122–4° (sealed capillary). (Found: Cl, 23.73; N, 8.50; Sn, 38.63. $C_{12}H_{16}Cl_4N_4Sn_2$ calcd.: Cl, 23.85; N, 9.41; Sn, 39.87 %.)

Separation of a redistribution reaction mixture

The following example is typical of the method used for separating products from a redistribution reaction.

Reaction of tetrakis(2-cyanoethyl)tin and tin(IV) bromide. The reaction was conducted under a nitrogen atmosphere. A mixture of tin(IV) bromide (18.4 g, 0.042 mole) and tetrakis(2-cyanoethyl)tin (14.1 g, 0.042 mole) was heated to 105° and maintained at this temperature for 5 h. The 1 : 1 $Sn(CH_2CH_2CN)_4 \cdot SnBr_4$ complex, which initially formed when the components were mixed, melted at 80° to a clear yellow liquid. At the end of the reaction period, the mixture was a thick, brown syrup. This syrup, after it had been cooled to 70°, was extracted with two 100 ml portions of boiling carbon tetrachloride. The white solid (3.8 g, 4 %) which crystallized from the cooled (5°) extracts had m.p. 76–78°. This product was identified as (2-cyanoethyl)tin tribromide by comparison of its infrared spectrum with that of an authentic sample and by mixed m.p. with authentic material[1].

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* Conducted under a nitrogen atmosphere.

To the syrupy residue from the carbon tetrachloride extraction was added 120 ml of water. Nearly all dissolved except for a small quantity of oil, which settled to the bottom of the flask. After separating the aqueous solution from the oil, the latter was collected, washed with water, and then dried. The oil (9.8 g, 69.5%) was identified as unreacted tetrakis(2-cyanoethyl)tin by its index of refraction (n_D^{22} 1.5330; lit.[7] n_D^{20} 1.5339) and infrared spectrum which was superimposible with that of the starting material.

The aqueous layer was transferred to a flask and 50 ml of acetone was added. To this solution was added 11.7 g (0.07 mole) of silver acetate, causing brown solids to precipitate. After stirring for 1 h, 15.6 g of a brown solid was collected and saved. The mother liquor was evaporated to dryness and a grey solid was obtained as residue. The latter was dissolved in boiling tetrahydrofuran (125 ml) and filtered while hot. To the filtrate, after cooling to room temperature, was added 300 ml of ethyl ether. The white solid which precipitated was filtered, washed with ethyl ether, and dried to give 2.5 g (12.8%), m.p. 150–1°. A mixed melting point with authentic tris(2-cyanoethyl)tin acetate[1] showed no depression. Its identity was further confirmed by comparing its infrared spectrum with that of an authentic sample.

The brown solid was washed with 25 ml of hot tetrahydrofuran, causing a loss of 2.9 g. To the tetrahydrofuran extract was added 75 ml of water and the solution was boiled until the tetrahydrofuran was removed. Sodium sulfide (1.56 g, 0.02 mole) in 10 ml of water was added slowly to the aqueous solution. A white solid precipitated and then redissolved upon the further addition of sodium sulfide. Acidification with 2.4 g (0.04 mole) of acetic acid reprecipitated the white solid. This solid was collected by filtration and then recrystallized from an acetone/methanol mixture. A total of 1.3 g (6%) was obtained, m.p. 173–5° [mixed melting point with an authentic sample of bis(2-cyanoethyl)tin sulfide[1] was not depressed). Its infrared spectrum was superimposible with that of the authentic sample, thus confirming its identity. See footnote *b*, Table 2, for a definition of how yields in this experiment were calculated.

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SUMMARY

Tetrakis(2-cyanoethyl)tin forms 1:1 complexes when it is allowed to react with either tin(IV) chloride or bromide in methylene chloride at room temperature, but not with tin(IV) fluoride, tin(IV) iodide, tin(IV) sulfate, and tin(IV) oxide. At elevated temperatures, these complexes undergo redistribution reactions by themselves, with added tetrakis(2-cyanoethyl)tin, or with added tin(IV) halide (Cl or Br). All possible redistribution products were obtained in poor to moderate yields, depending on experimental conditions. Regardless of the stoichiometry of the reactants,

tris(2-cyanoethyl)tin bromide is the major product when tin(IV) bromide is used. The infrared nitrile absorptions for the complexes and tetrakis(2-cyanoethyl)tin are reported and discussed.

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