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XI.* (2-CYANOETHYL)TIN BROMIDES

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INTRODUCTION

Although many symmetrical tetraalkyltin compounds have been synthesized[1], the vast majority contain no functional substituents on the alkyl chains. In 1959, Tomilov and Kaabak[2] reported the synthesis of tetrakis(2-cyanoethyl)tin by electrolysis of an aqueous alkaline solution of acrylonitrile using a tin cathode.

Since that time, several other (2-cyanoethyl)tin derivatives have been reported. Kaabak and Tomilov[3] described the preparation of all four tris(2-cyanoethyl)tin halides by cleavage of $(NCCH_2CH_2)_4Sn$ with the appropriate halogen, while Matsuda and Kikkawa[4] reported the synthesis of bis(2-cyanoethyl)tin dibromide and a diiodide by the direct reaction of 2-bromo- and 2-iodopropionitrile with metallic tin. The diiodide was characterized as a sharp melting solid, but the dibromide could only be isolated as an impure, viscous liquid.

In the present paper, the successful syntheses of two new (2-cyanoethyl)tin derivatives, bis(2-cyanoethyl)tin dibromide and (2-cyanoethyl)tin tribromide, are reported. Also, the infrared absorption band(s) in the nitrile region (4.3–4.5 μ) for the three (2-cyanoethyl)tin bromides are discussed and an attempt is made to correlate these results with molecular weight data.

RESULTS AND DISCUSSION

Bis(2-cyanoethyl)tin dibromide (I) was prepared by the following unambiguous three-step synthesis (1–3). Both intermediates, (I) and (II), were used without further purification.

$$(C_6H_5)_2SnCl_2 + LiAlH_4 \xrightarrow{Et_2O} (C_6H_5)_2SnH_2 \quad (I) \qquad (1)$$

$$(C_6H_5)_2SnH_2 + 2\ CH_2{=}CHCN \xrightarrow{70°} (C_6H_5)_2Sn(CH_2CH_2CN)_2 \quad (II) \qquad (2)$$

$$(C_6H_5)_2Sn(CH_2CH_2CN)_2 + 2\ Br_2 \xrightarrow{CHCl_3} (NCCH_2CH_2)_2SnBr_2 \quad (III) + 2\ C_6H_5Br \qquad (3)$$

The dibromide (III) is a crystalline solid (m.p. 178° dec.). The synthesis gave overall yields which ranged from 9 to 45%, averaging 32%. We believe that the low and erratic yields for the dibromide are primarily due to the inherent instability of diphenyltin dihydride[5]. It is obvious that the viscous liquid isolated by Matsuda

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* For Part X, see preceding paper.

and Kikkawa[4] was not the dibromide. We repeated the procedure of Matsuda and Kikkawa and were not able to isolate any bis(2-cyanoethyl)tin dibromide.

An analogous scheme was utilized for the synthesis of (2-cyanoethyl)tin tribromide (IV):

$$(C_6H_5)_3SnCH_2CH_2CN + 3\ Br_2 \rightarrow \underset{(IV)\ 76\%}{NCCH_2CH_2SnBr_3} + 3\ C_6H_5Br$$

With the exception of the recently reported synthesis of cyclohexyltin tribromide by the reaction of triphenylcyclohexyltin with bromine[6], preparatively useful cleavage of three tin–carbon bonds by halogens is rare. In fact, when attempts were made to cleave only three tin–carbon bonds in R_4Sn (R = alkyl or aryl), the reaction did not stop at the $RSnX_3$ (R = alkyl or aryl) stage, but proceeded directly to the tetrahalide[7]. The preferential cleavage by halogens of unsubstituted alkyl (or aryl) groups in organotin compounds containing either a 2-cyanoethyl or a 3-cyanopropyl group is well-known[7]. The resistance of the 2-cyanoethyl or 3-cyanopropyl group toward cleavage of halogens is probably due to the inductive effect of the cyano group.

The infrared spectra of all three cyanoethyltin bromides have been investigated. Of particular interest were the absorption bands in the nitrile region. Complexing aliphatic or aromatic nitriles with tin tetrachloride is known to cause an increase in the stretching frequency of the $-C{\equiv}N$ band relative to that for the free nitrile[8,9] and this has been attributed to coordination of the lone pair of electrons on the nitrile nitrogen by the Lewis acid, tin tetrachloride[9]. An organotin compound containing a 2-cyanoethyl group has both acidic and basic sites (in the Lewis sense) in the same molecule. To determine whether the (2-cyanoethyl)tin bromides form intermolecular complexes, similar to the type described above, was a major purpose of the present investigation. Table 1 summarizes the infrared absorptions in the nitrile region and the molecular weight data for all three bromides.

TABEL 1

INFRARED AND MOLECULAR WEIGHT DATA

Compound	*Molecular weight*			*$-C{\equiv}N$ stretching frequency*	
	Solvent	*Calcd.*	*Found*	*Solvent*	*cm^{-1}*
$(NCCH_2CH_2)_4Sn$	$CHCl_3$	334.7	320	Neat	2242
$(NCCH_2CH_2)_3SnBr$	THF	360.6	334	Nujol	2268, 2247
				THF	2247
$(NCCH_2CH_2)_2SnBr_2$	THF	386.5	370	Nujol	2252
				THF	2252
$NCCH_2CH_2SnBr_3$	Benzene	412.4	400	Nujol	2283
				Benzene	2283
				THF	2247

The presence of a doublet in the nitrile region for tris(2-cyanoethyl)tin bromide (nujol mull), strongly indicates that in the solid state intermolecular complexes are present. These complexes probably consist of a chain of monomer units in which a nitrile group of one molecule is coordinated to a tin atom of another, etc. Based on previous infrared studies reported for the tin tetrachloride–organonitrile com-

complexes[8,9] the higher frequency band is assigned to intermolecular complexes of the bromide with itself, while the lower frequency band is assigned to the monomeric or uncomplexed species. As this assignment would require, the higher frequency band disappears when the spectrum is measured in tetrahydrofuran (THF). This is a consequence of the donor properties of THF. Upon solution, the THF would compete with the nitrile for coordination sites and destroy the intermolecular complex. In agreement with the infrared behavior, the molecular weight of the monobromide in THF is that of the monomer. The low solubility of the compound in non-donor solvents precluded molecular weight determinations in such media.

Contrary to our expectations, the data in Table 1 indicates that the dibromide does not form complexes with itself. Only one nitrile band is found regardless of whether the infrared data was obtained for the solid state (nujol mull) or as a tetrahydrofuran solution. Furthermore, it is assignable to an uncoordinated nitrile. The molecular weight of the dibromide in THF is that expected for monomer and is in agreement with this interpretation of the infrared data. Again low solubility in non-donor solvents prevented molecular weight measurements. No ready explanation is available for this apparent anomaly.

The infrared data shows only one nitrile peak for (2-cyanoethyl)tin tribromide in the solid state (nujol mull), in benzene, or in THF. However, the nitrile stretching frequency in benzene solution or in the solid state (nujol mull) is 36 cm^{-1} higher than in tetrahydrofuran. The higher frequency vibration observed in non-donor media is assigned to intermolecular complexes of the tribromide with itself while the normal nitrile frequency, which is observed in tetrahydrofuran solution, is assigned to the uncomplexed or monomeric species. The basis for these assignments is the same as for the monobromide given above.

The tribromide, as is typical of this type of compound, has good aromatic hydrocarbon solubility. We were able to achieve a concentration in benzene (*ca.* 10 w/v %) which gave usable spectra. At *this* concentration, the tribromide is complexed in benzene solution. However within the concentration range used in the molecular weight study ($<$ 1 w/w %) the intermolecular complex is apparently completely dissociated, even in the non-donor solvent benzene.

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 (Beckman Instruments, Inc., Fullerton, Cal.).

Tetrakis(2-cyanoethyl)tin

Tetrakis(2-cyanoethyl)tin was prepared by the electrolytic method described by Tomilov and Kaabak[2]. It was crystallized from methylene chloride at −78°.

Tris(2-cyanoethyl)tin bromide

This compound was prepared according to the procedure described by Kaabak and Tomilov[3]. Yields for five preparations ranged from 46–74%, averaging 60%, m.p. 103–4° (lit.[3] 105–105.5°).

Bis(2-cyanoethyl)tin dibromide

(*a*) Diphenyltin dihydride was prepared using the method outlined by Van der Kerk and co-workers[10]. From 103.1 g (0.30 mole) of diphenyltin dichloride, 67.1 g of "crude" diphenyltin dihydride was obtained as a cloudy, yellowish liquid. The entire product was used without further purification. (*b*) Under a nitrogen atmosphere, a mixture of diphenyltin dihydride (67.1 g), hydroquinone (100 mg), and acrylonitrile (37.1 g, 0.70 mole) was heated at 70° for 5.75 h. After the reaction mass had cooled to room temperature, acetone (150 ml) was added and the mixture filtered with water suction. A green solid (2.2 g) was filtered off and discarded. The filtrate was concentrated at reduced pressure to leave as a cloudy yellow liquid "crude" diphenylbis(2-cyanoethyl)tin (77.3 g). The entire product was used without further purification. (*c*) To a solution of "crude" diphenylbis(2-cyanoethyl)tin (77.3 g) in 200 ml of chloroform was added a solution of bromine (62.0 g, 0.388 mole) in 250 ml of chloroform over a 40-min period. A moderate exotherm was observed. When the mid-point of the bromine addition was reached, the clear yellow solution turned turbid, and with further additions of bromine, the turbidity increased and a white solid formed. The mixture was filtered and the white solid, after washing with chloroform, was air dried to give 41.5 g which represents an overall 35.8% yield of bis(2-cyanoethyl)tin dibromide based on the quantity of diphenyltin dichloride used in step (*a*) above; m.p. 172–175° (dec.). After repeated recrystallizations from a tetrahydrofuran/hexane solvent pair the melting point was raised to a constant value of 178–182° (dec.). (Found: Br, 40.5; N, 7.23; Sn, 30.49; mol. wt. in tetrahydrofuran, 370. $C_6H_8Br_2N_2Sn$ calcd.: Br, 41.35; N, 7.24; Sn, 30.71%; mol. wt., 386.5.)

(2-Cyanoethyl)tin tribromide

(*a*) Triphenyltin hydride was prepared by reducing triphenyltin chloride with lithium aluminum hydride according to the procedure outlined by Van der Kerk and co-workers[9]. From 455.0 g (1.18 moles) of triphenyltin chloride, 392.1 g of "crude" triphenyltin hydride was obtained as a slightly hazy yellow liquid. This material was used without further purification in the preparation of triphenyl(2-cyanoethyl)tin. (*b*) Triphenyl(2-cyanoethyl)tin was prepared by reacting "crude" triphenyltin hydride (392.1 g) with acrylonitrile (118.7 g, 2.24 moles) according to the method of Van der Kerk and co-workers[11]. An overall yield of 55% was obtained for triphenyl(2-cyanoethyl)tin based on the triphenyltin chloride used in the above step, m.p. 92–93° (lit.[11] 93–94°). (*c*) To a warm (40°) solution of triphenyl(2-cyanoethyl)tin (75.0 g, 0.19 mole) in carbon tetrachloride (150 ml) was added slowly over a 50-min period a solution of bromine (95.9 g, 0.60 mole) in the same solvent (150 ml). A strong exotherm was observed and the solution rapidly discharged the bromine color until about 50% of the bromine solution had been added. At this point, external heat was applied so that the solution refluxed while the bromine addition continued. After all the bromine had been added, the reaction mixture was refluxed for an additional 90 min and then allowed to stand overnight during which time the product crystallized out. It was collected by filtration, washed several times with fresh portions of carbon tetrachloride, and then was dried in an air circulation oven at 50°

to give 48.0 g of (2-cyanoethyl)tin tribromide, m.p. 75–76°. A second crop of crystals (10.3 g; m.p. 75–77°) was obtained by evaporating the mother liquor to about one-third of its original volume and then cooling the solution in a refrigerator. Total weight of (2-cyanoethyl)tin tribromide isolated was 58.3 g (76% yield). Recrystallization of the combined crops from hot carbon tetrachloride did not change the melting point. (Found: Br, 57.6; N, 3.41; Sn, 28.65; mol.wt. in benzene, 400. $C_3H_4Br_3NSn$ calcd.: Br, 58.1; N, 3.40; Sn, 28.78%; mol.wt., 412.4.)

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SUMMARY

The syntheses of bis(2-cyanoethyl)tin dibromide and (cyanoethyl)tin tribromide by reaction of bromine with diphenylbis(2-cyanoethyl)tin and triphenyl-(2-cyanoethyl)tin, respectively, in an inert solvent are reported. Based on the nitrile absorption bands in nujol, it is concluded that tris(2-cyanoethyl)tin bromide and (2-cyanoethyl)tin tribromide, but not bis(2-cyanoethyl)tin dibromide, are associated in the solid state. The nature of these associations are discussed in detail. Molecular weight determinations show that tris(2-cyanoethyl)tin bromide and bis(2-cyanoethyl)tin dibromide are monomeric in tetrahydrofuran and that (2-cyanoethyl)tin tribromide is monomeric in benzene.

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