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XII. NEW (2-CYANOETHYL)TIN DERIVATIVES

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INTRODUCTION

In a previous paper[1], we reported the synthesis of bis(2-cyanoethyl)tin dibromide and (2-cyanoethyl)tin tribromide. The present paper discusses the use of these two bromides and tris(2-cyanoethyl)tin bromide[2] as starting materials in the preparation of six new (2-cyanoethyl)tin derivatives.

RESULTS AND DISCUSSION

A. $(NCCH_2CH_2)_3SnX$

Tris(2-cyanoethyl)tin acetate (I) was prepared by treating tris(2-cyanoethyl)tin bromide with equimolar quantities of silver or thallous acetate in aqueous acetone (eqn. 1).

$$(NCCH_2CH_2)_3SnBr + CH_3CO_2M \rightarrow \underset{(I)}{(NCCH_2CH_2)_3SnO_2CCH_3} + MBr \qquad (M = Ag \text{ or } Tl) \quad (1)$$

We prefer thallous acetate to silver acetate as a source of the acetate moiety because blackening of the product complicated the silver acetate preparations.

Tris(2-cyanoethyl)tin hydroxide, (II), was prepared by adding a stoichiometric quantity of thallous oxide suspended in water to a solution of tris(2-cyanoethyl)tin bromide in acetone (eqn. 2). Elemental analysis indicated that the product was a monohydrate $(NCCH_2CH_2)_3SnOH \cdot H_2O$. The same product may be obtained by substituting silver oxide for thallous oxide;

$$2\,(NCCH_2CH_2)_3SnBr + Tl_2O + 2\,H_2O \rightarrow 2\,\underset{(II)}{(NCCH_2CH_2)_3SnOH \cdot H_2O} + 2\,TlBr \quad (2)$$

However, as in the preparation of the acetate, the use of silver compounds caused blackening of the product. Under mild conditions the hydroxide (II) was readily converted into the corresponding acetate (I) in 94% yield.

B. $(NCCH_2CH_2)_2SnX_2$

Basic hydrolysis of bis(2-cyanoethyl)tin dibromide with either an excess of ammonia or sodium hydroxide did not produce the corresponding oxide $(NCCH_2CH_2)_2SnO$, or the dihydroxide, $(NCCH_2CH_2)_2Sn(OH)_2$. Instead, an intermediate product, 1,1,3,3-tetrakis(2-cyanoethyl)-1,3-dihydroxydistannoxane, (III), was isolated in high yield (eqn. 3).

$$2\,(NCCH_2CH_2)_2SnBr_2+4\,NH_3+3H_2O \rightarrow \underset{\text{(III)}}{[(NCCH_2CH_2)_2SnOH]_2O}+4\,NH_4Br \qquad (3)$$

In contrast to our result, unsubstituted dialkyltin dihalides, *e.g.*, $(C_2H_5)_2SnCl_2$, yield dialkyltin oxides (R_2SnO), upon hydrolysis with excess base[3]. Intermediate products, formed by the hydrolysis of dialkyltin dihalides under mild conditions, have been isolated[4]. They have consisted of two types, $[(R_2SnX)_2O]_2$ and $[XR_2SnOSnR_2OH]_2$. The addition of base to $[XR_2SnOSnR_2OH]_2$ does not produce $(R_2SnOH)_2O$, but instead yields the corresponding dialkyltin oxide R_2SnO.

Molecular weight data for (III) could not be obtained because it is insoluble in common solvents. In the absence of X-Ray and molecular weight data, the tentative evidence for the structure postulated for (III) was based on (*a*) elemental analysis and (*b*) its facile conversion into derivatives which have the same skeletal features (see below). It appears that (III) is the first example of a compound having a distannoxane grouping in addition to a hydroxyl group bonded to each of the two tin atoms.

When 1,1,3,3-tetrakis(2-cyanoethyl)-1,3-dihydroxydistannoxane (III) is treated with the stoichiometric quantity of 2-ethylhexanoic acid with the object of preparing $(NCCH_2CH_2)_2Sn(O_2CC_7H_{15})_2$ (IV), the expected product was not obtained and only 60–67% of the theoretical quantity of water could be realized. The product actually isolated was the basic carboxylate, $[(NCCH_2CH_2)_2SnO_2CCH(C_2H_5)C_4H_9]_2O$ (V), which was shown by molecular weight data to be monomeric in chloroform solution. In contrast to our result, it has previously been shown that basic organotin carboxylates are dimeric in solution[5]. Attempts to prepare the dicarboxylate (IV) under anhydrous conditions were unsuccessful; the product isolated contained free carboxylic acid (based on infrared data). It appears that products having the structure (IV) are either incapable of existence or, if formed, are very sensitive to adventitious moisture.

In contrast to carboxylic acids, isooctyl thioglycolate reacts with (III) to yield bis(2-cyanoethyl)tin bis(isooctyl thioglycolate) (VI) and 96% of the water required on eqn. (4) was obtained.

$$\text{(III)}+4\,HSCH_2CH_2CO_2\text{-iso-}C_8H_{17} \rightarrow 3\,H_2O+(NCCH_2CH_2)_2Sn(SCH_2CO_2\text{-iso-}C_8H_{17})_2 \qquad (4)$$

The dimercaptide also may be formed by treating bis(2-cyanoethyl)tin dibromide with the stoichiometric quantity of isooctyl thioglycolate in the presence of an acid acceptor, triethylamine. The differences in the type of products obtained when the stannoxane (III) is treated with a carboxylic acid or a mercaptan may be explained on the basis of the greater hydrolytic stability of the tin–sulfur bond as compared to the tin–oxygen bond[6].

The reaction of bis(2-cyanoethyl)tin dibromide with sodium sulfide in aqueous solution (molar ratio 1:2) initially precipitated bis(2-cyanoethyl)tin sulfide, (IX), which redissolved, yielding a clear solution presumably containing the bis(2-cyanoethyl)dithiostannate dianion, (VII). Organothiostannate anions such as (VII) have previously been postulated as intermediates in the preparation of dialkyl- or diaryltin sulfides when the corresponding oxides reacted with sulfide ion and the resulting solutions were acidified[6].

Acidification of the solution containing the organothiostannate dianion (VII) with acetic acid immediately precipitated bis(2-cyanoethyl)tin sulfide, (IX), (86%) and hydrogen sulfide was simultaneously evolved. Presumably, the dithiol (VIII) is the intermediate formed after acidification[6]; however, it is very unstable and decomposes immediately into the dialkyltin sulfide, (IX), which is isolated as the cyclic trimer, and hydrogen sulfide (eqn. 5).

$$\begin{array}{ll}
(NCCH_2CH_2)_2SnBr_2 + 2\,S^{2-} \xrightarrow{H_2O} \underset{(VII)}{[(NCCH_2CH_2)_2SnS_2]^{2-}} + 2\,Br^- & (5) \\
3\,(VII) + 6\,CH_3CO_2H \xrightarrow{H_2O} 3\,\underset{(VIII)}{[(NCCH_2CH_2)_2Sn(SH)_2]} + 6\,CH_3CO_2^- & \\
\qquad\qquad\qquad\qquad\qquad \text{spontaneous}\downarrow & \\
\qquad\qquad\qquad\qquad\qquad \underset{(IX)}{[(NCCH_2CH_2)_2SnS]_3}\downarrow + 3\,H_2S\uparrow &
\end{array}$$

EXPERIMENTAL

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

The preparations of tris(2-cyanoethyl)tin bromide[2], bis(2-cyanoethyl)tin dibromide[1], and 2-(cyanoethyl)tin tribromide[1] have been described previously.

Preparation of tris(2-cyanoethyl)tin acetate (I)

To a solution of tris(2-cyanoethyl)tin bromide (137.0 g, 0.38 mole) in 500 ml of acetone was added with stirring a solution of 100.0 g (0.38 mole) of CH_3CO_2Tl in 100 ml of water. Immediately, a yellow precipitate of TlBr formed. After stirring for an additional 15 min period, thallous bromide was removed by filtration. The clear, colorless mother liquor gave a negative Br^- test. Solvents were removed from the mother liquor under reduced pressure. Tris(2-cyanoethyl)tin acetate (129.0 g) was obtained in quantitative yield. An analytically pure sample was obtained by dissolving the acetate in tetrahydrofuran and reprecipitating it with ethyl ether, m.p. 150–151°. (Found: N, 12.21; Sn, 35.17. $C_{11}H_{15}N_3O_2Sn$ calcd.: N, 12.36; Sn, 34.94%.)

Preparation of tris(2-cyanoethyl)tin hydroxide monohydrate (II)

To a stirred solution of tris(2-cyanoethyl)tin bromide (19.8 g, 0.055 mole) in 350 ml of acetone was added rapidly a suspension of 11.9 g (0.056 mole) of Tl_2O in 60 ml of water. After stirring for an additional 35 min, conversion of the brownish-black Tl_2O to yellow TlBr was apparent. The insoluble TlBr was filtered off and the solvents (negative Br^- test) were removed from the filtrate at reduced pressure. A 92% yield of $(NCCH_2CH_2)_3SnOH \cdot H_2O$ (16.0 g) was obtained as residue, m.p.

103–5° (cloudy). Recrystallization from acetone containing 1% water* yielded the pure compound, m.p. 103–4°. (Found: C, 34.78; H, 4.26; N, 13.40; Sn, 38.13. $C_9H_{15}N_3O_2Sn$ calcd.: C, 34.21; H, 4.75; N, 13.30; Sn, 37.60%.)

1,1,3,3-*Tetrakis*(2-*cyanoethyl*)-1,3 *dihydroxydistannoxane* (*III*)

A solution of 4.2 g (0.25 mole) of ammonia in 100 ml of water was added slowly to a solution of 19.3 g (0.05 mole) of bis(2-cyanoethyl)tin dibromide in 100 ml of water, which had been cooled to 10–15°. The white solids which precipitated initially later turned light pink. After stirring for an additional 10 min, the mixture was filtered with suction, and the filter cake was washed alternately with tetrahydrofuran and water until a portion of the wash water gave a negative Br^- test. 1,1,3,3-Tetrakis-(2-cyanoethyl)-1,3-dihydroxydistannoxane (10.5 g, 83%) was collected, m.p. 195° (dec.). (Found: N, 11.22; Sn, 46.96. $C_{12}H_{18}N_4O_3Sn_2$ calcd.: N, 11.11; Sn, 47.16%.)

1,1,3,3-*Tetrakis*(2-*cyanoethyl*)-1,3-bis(2-*ethyl*-*n*-*hexanoyloxy*)*distannoxane*

A mixture of 1,1,3,3-tetrakis(2-cyanoethyl)-1,3-dihydroxydistannoxane (25.2 g, 0.05 mole), 2-ethylhexanoic acid (28.8 g, 0.20 mole), and benzene (350 ml) was refluxed for 2 h, during which time 1.8 ml (100%) of water was collected in a Dean Stark trap. The resulting yellow, slightly cloudy solution was filtered. Benzene was removed from the filtrate at reduced pressure to leave a yellow liquid (48.7 g), which solidified to a waxy solid when cooled to 5°; this product melted over the range 45–151°. Recrystallization from a tetrahydrofuran/hexane solvent pair yielded 27.7 g (73%) of 1,1,3,3-tetrakis(2-cyanoethyl)-1,3-bis(2-ethyl-n-hexanoyloxy)distannoxane as a white crystalline solid, m.p. 154–5° (dec.). Repeated recrystallizations from the same solvent pair did not change the melting point or mixed melting point (with sample from a previous recrystallization). (Found: N, 7.69; Sn, 32.06; mol. wt. in chloroform, 730. $C_{28}H_{46}N_4O_5Sn_2$ calcd.: N, 7.41; Sn, 31.43%; mol. wt., 755.)

Bis(2-*cyanoethyl*)*tin di*(*isooctyl thioglycolate*) (*VI*)

A mixture of 21.8 g (0.043 mole) of 1,1,3,3-tetrakis(2-cyanoethyl)-1,3-dihydroxydistannoxane, 36.7 g (0.18 mole) of isooctyl thioglycolate, and 350 ml of benzene was refluxed for 2 h, during which time 2.3 ml (96%) of water was collected in a Dean Stark trap. After the solution had cooled to room temperature, it was filtered in order to remove a small amount of insoluble material. Benzene was removed from the filtrate at reduced pressure. Bis(2-cyanoethyl)tin di(isooctyl thioglycolate) (53.7 g) was obtained as a clear yellow liquid in 94.4% yield, n_D^{25} 1.5215. (Found: N, 4.25; S, 10.27; Sn, 17.89. $C_{26}H_{46}N_2O_4S_2Sn$ calcd.: N, 4.43; S, 10.12; Sn, 18.76%.)

Preparation of bis(2-*cyanoethyl*)*tin sulfide* (*IX*)

To a solution of 34.7 g (0.09 mole) of bis(2-cyanoethyl)tin dibromide in 170 ml of water was added, with stirring, a solution of 14.2 g (0.18 mole) of sodium sulfide in 75 ml of water. The white precipitate which formed originally dissolved upon the further addition of sodium sulfide to yield a clear solution. Over a 2-min period,

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* The product is insoluble in anhydrous acetone or water separately. Addition of a small amount of water (*ca.* 1%) to acetone facilitates recrystallization. In certain acetone/water mixtures, the product is soluble even at room temperature.

acetic acid (22.0 g, 0.37 mole) in 50 ml of water was added, causing the white solid to reprecipitate and hydrogen sulfide to be evolved. The mixture was filtered and the filter cake was washed with water until a small portion of the wash water gave only a slightly yellow coloration, but no precipitate of AgBr, when acidified $AgNO_3$ was added. A total of 20.2 g (86 %) of bis(2-cyanoethyl)tin sulfide was obtained, m.p. 163–5°. Recrystallization from an acetone/methanol solvent pair gave an analytical sample of m.p. 173–5°. [Found: N, 10.80; S, 12.45; Sn, 45.76; mol. wt. in tetrahydrofuran, 740. $(C_6H_8N_2SSn)_3$ calcd.: N, 10.82; S, 12.37; Sn, 45.84 %; mol. wt. for trimer, 776.]

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SUMMARY

Six new (2-cyanoethyl)tin derivatives are reported for the first time. The reaction of tris(2-cyanoethyl)tin bromide with thallous oxide in aqueous acetone yields the corresponding hydroxide, as a monohydrate. Basic hydrolysis of bis(2-cyanoethyl)tin dibromide with excess aqueous ammonia or sodium hydroxide does not produce the corresponding oxide or dihydroxide, but an intermediate product, 1,1,3,3-tetrakis(2-cyanoethyl)-1,3-dihydroxydistannoxane. The reaction of bis(2-cyanoethyl)tin dibromide with excess aqueous sodium sulfide initially precipitates white solids which dissolve upon the further addition of sulfide ion. Only after acidification with acetic acid is the corresponding sulfide, $[(NCCH_2CH_2)_2SnS]_3$ obtained. In addition to the compounds described above, the following were also prepared: tris(2-cyanoethyl)tin acetate; 1,1,3,3-tetrakis(2-cyanoethyl)-1,3-bis(2-ethylhexanoyloxy)distannoxane; and bis(2-cyanoethyl)tin di(isooctyl thioglycolate).

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