(threonine) residues of the peptide chain is cleaved according to the mechanism of $\beta$-elimination. No indication for such a mechanism was obtained when seryl-$N$-acetylgalactosaminidase acted on the susceptible bond in NANA-free OSM. The result of a more detailed study of the mechanism of the enzymatic action is shown in Fig. 1.

![Fig. 1. Enzymatic release of N-acetylated hexosamine from NANA-free OSM with time in relation to the absorbance at 241 μM. The assay contained 0.8 ml NANA-free OSM solution (see text), 0.6 ml 0.1 M citrate buffer (pH 4.8) and 1.0 ml seryl-$N$-acetylgalactosaminidase solution (0.65 milliunits). The figures shown are corrected for substrate and enzyme controls.](image_url)

Discussion of results

The experiments concerned with the action of seryl-$N$-acetylgalactosaminidase on esterified OSM and NANA-free OSM would indicate that the known resistance of native OSM to this enzyme results from steric hindrance by the voluminous $N$-acytyleunamic acid unit rather than from the negative charge at its carboxyl group. From the result shown in Fig. 1 a $\beta$-elimination type of reaction as mechanism of the action of seryl-$N$-acetylgalactosaminidase can be excluded with confidence since the release of 395 μM N-acetylgalactosamine was not coincided by any light absorbance at 241 μM. At this wavelength derivatives of $\alpha$-amino acrylic acid, formed for instance by $\beta$-elimination of O-glycosylated serine derivatives, are known to absorb strongly.

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8 See, for instance, G. J. M. van der Kerk and J. G. Luijten, J. appl. Chem. 6, 93 [1956].

Disproportionation of a Triorganotin Ester

DIETMAR SEYFERTH and JAMES M. BURLITCH

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

The thermal disproportionation of triorganotin halides, oxides and hydroxides [Eq. (1)] is a well-known reaction in organotin chemistry.

$$2 R_2 SnX \rightarrow R_2 Sn + R_2 SnX_3 \quad (1)$$

However, a corresponding reaction of a triorganotin ester has, to the best of our knowledge, not been recorded to date. We describe here some fragmentary results of a study (which has been discontinued) that show that at suitably high temperatures, triorganotin esters also can undergo such disproportionation.

Trimethyl- and triethyltin $o$-bromobenzoate were prepared with the intention of studying the possibility of their thermal decarboxylation to give $o$-bromophenyltritylalkyl compounds. Such decarboxylations have been found to serve in other cases in the synthesis of tincarbon bonds. When trimethyltin $o$-bromobenzoate was heated in a melting point capillary to its m.p. of 209 to 210$^\circ$, strong effervescence was observed at the melting point. However, a pyrolysis of this compound carried out on a 10 g scale showed that the effervescence was due to the evolution of the volatile (b.p. 78$^\circ$) tetramethyltin rather than of carbon dioxide. The major products of the pyrolysis were found to be tetramethyltin, $\text{sym-bis}(o$-bromobenzoato)tetramethylstannoxane and $o$-bromobenzoic acid. The reaction path below serves to explain the formation of these products.

![Chemical structure](image_url)

It may be noted that partial hydrolysis of diorganotin diacylates in solution to the corresponding stannoxanes occurs very readily, and that special precautions are required for the isolation of pure diorganotin diacylates.

Experimental

Preparation of Organotin $o$-Bromobenzoates. Into a 500 ml M o r t o n flask equipped with a high-speed stirrer and a cold finger condenser was placed 4.86 g (20 mmoles) of trimethyltin bromide and 125 ml of 95% acetic acid. The solution was heated to 210$^\circ$, the mixture was then rapidly transferred to a 200 ml round-bottom flask equipped with a high-speed stirrer and a cold finger condenser. The reaction was quenched with a cold water jet. The reaction product was then treated with 50 ml of a cold water jet and the mixture was allowed to cool. The residue was washed with diethyl ether and air-dried. The crude product was recrystallized from methanol to give white needles, m. p. 210$^\circ$ (melting point capillary).
ethanol. Silver o-bromobenzoate \(^3\) (6.16 g, 20 mmoles) was added, with stirring, in subdued light. The flask was wrapped in aluminum foil to exclude light, and the reaction mixture was stirred for 8 hours at room temperature. It then was filtered and the residue was washed with 95% ethanol. The filtrate was concentrated to 75 ml and stored at 0° for 24 hours. The white, needle-like crystals which formed were filtered and dried, giving trimethyltin o-bromobenzoate, 3.5 g (48%), m.p. 208—210° (with effervescence). Further purification of the product was effected by sublimation at 120° (0.001 mm). The sublimate had m.p. 209—210° (with effervescence); \(\nu_{\text{C-O}}\) 1570 cm\(^{-1}\). Found: C, 32.83; H, 3.71; Br, 21.97. Calcd. for C\(_{19}\)H\(_{19}\)O\(_3\)BrSn: C, 33.01; H, 3.60; Br, 21.90.

Triethyltin o-bromobenzoate was prepared in a similar manner in 70% yield. M.p. of a sublimed (90° at 0.001 mm) sample was 101.5—102.5°; \(\nu_{\text{C-O}}\) 1645 cm\(^{-1}\). This material effervesced only slowly when heated to 150—200°. Found: C, 38.34; H, 4.84; Br, 19.70. Calcd. for C\(_{23}\)H\(_{23}\)OBrSn: C, 38.46; H, 4.71; Br, 19.68.

**Sym-bis(o-bromobenzoxyloxy)tetrakisdimethylstannoxane.**

An authentic sample was prepared in the following manner. A solution of 10.05 g (50 mmoles) of o-bromobenzoic acid in 40 ml of 95% ethanol was neutralized (to pH 7) with 60 ml of 1 M NH\(_4\)OH. Nitric acid then was added to adjust the pH to 5. A solution of 5.24 g (25 mmoles) of dimethyltin dichloride in 50 ml of water was added with stirring. The resulting white precipitate was recrystallized from benzene/hexane to give 4.44 g of product, m.p. 254—256°. This product very likely is derived from dimethyltin oxide, formed on the chromatographic column by hydrolysis of the original dimethyltin ester.

Elution of the material remaining on the column was continued using 20% ethyl acetate in chloroform. After six clean 15 ml fractions, a total of 2.0 g of white solid, m.p. 146—148°, was obtained upon evaporation of the following thirteen 15 ml fractions. The m.p., after recrystallization, was 148.5—149.5°. Its infrared spectrum (KBr) was identical to that of sym-bis(o-bromobenzoxyloxy)tetrakisdimethylstannoxane and a mixture m.p. with authentic material was not depressed.

**Pyrolysis of Triethyltin o-Bromobenzoate.** A vertical pyrolysis tube with a water-cooled cold finger was used, which led to two cold traps in series, the first at —78°, the second at —196°. Ten g (27.5 mmoles) of the tin compound was charged into the tube and the system was flushed with nitrogen and evacuated to 40 mm. The tube contents were heated to 230° for 6 hours. Starting material which sublimed onto the cold finger was tapped loose periodically. During the pyrolysis, the molten solid initially evolved a liquid with much effervescence and then slowly turned orange-brown while occasionally evolving bubbles of gas.

Unconverted starting material (0.2 g) was sublimed from the solid remaining. The fluorescent pyrolysis product, 6.6 g, m.p. 138—142°, was powdered prior to further work-up.

The —78° trap contained ca. 3 ml of clear liquid. This was distilled at atmospheric pressure, giving 1.18 g of distillate, b.p. 79°, \(n_2^0\) 1.4384 (lit. \(n_2^0\) 1.4386 for tetramethyltin, b.p. 78°). Gas-liquid partition chromatography (General Electric Co. SE-30 on Chromosorb P) showed it to be essentially pure, containing only a trace of trimethyltin bromide. Only a few very small droplets of liquid were found in the liquid nitrogen trap.

A 4.6 g portion of the solid pyrolysis product was dissolved in chloroform and chromatographed on 100 g of Silica Gel in a 48 mm diameter column. The initial elution was accomplished with 1:1 chloroform-hexane. The rapid progress of the fluorescent component could be followed in the light of a filtered ultraviolet lamp. The eluted fractions were concentrated to 10 ml and cooled to give 1.2 g of solid. Recrystallization from chloroform/hexane gave white, crystalline solid with m.p. 254—256°. Its infrared spectrum (KBr) was identical to that of sym-bis(o-bromobenzoxyloxy)tetrakisdimethylstannoxane and a mixture m.p. with authentic material was not depressed.

**Pyrolysis of Trimethyltin o-Bromobenzoate.** The —78° trap contained ca. 3 ml of clear liquid. This was distilled at atmospheric pressure, giving 1.18 g of distillate, b.p. 79°, \(n_2^0\) 1.4384 (lit. \(n_2^0\) 1.4386 for tetramethyltin, b.p. 78°). Gas-liquid partition chromatography (General Electric Co. SE-30 on Chromosorb P) showed it to be essentially pure, containing only a trace of trimethyltin bromide. Only a few very small droplets of liquid were found in the liquid nitrogen trap.

A 4.6 g portion of the solid pyrolysis product was dissolved in chloroform and chromatographed on 100 g of Silica Gel in a 48 mm diameter column. The initial elution was accomplished with 1:1 chloroform-hexane. The rapid progress of the fluorescent component could be followed in the light of a filtered ultraviolet lamp. The eluted fractions were concentrated to 10 ml and cooled to give 1.2 g of solid. Recrystallization from chloroform/hexane gave white, crystalline solid with m.p. 254—256°. Its infrared spectrum (KBr) was identical to that of sym-bis(o-bromobenzoxyloxy)tetrakisdimethylstannoxane and a mixture m.p. with authentic material was not depressed.

Elution of the material remaining on the column was continued using 20% ethyl acetate in chloroform. After six clean 15 ml fractions, a total of 2.0 g of white solid, m.p. 146—148°, was obtained upon evaporation of the following thirteen 15 ml fractions. The m.p., after recrystallization, was 148.5—149.5°. Its infrared spectrum and a mixture m.p. showed it to be o-bromobenzoic acid.

The material remaining on the column was removed by elution, first with pyridine/chloroform and then with acetic acid/chloroform, to give 1.0 g of white solid, m.p. 237—240°. This material was identified as sym-bis(acetoxy)tetrakisdimethylstannoxane by means of its infrared spectrum (KBr) and by mixture m.p. (undepressed) with an authentic sample of m.p. 237—239° (lit. \(m.p.\) 240°). This product very likely is derived from dimethyltin oxide, formed on the chromatographic column by hydrolysis of the original dimethyltin ester.

This experiment demonstrates qualitatively that disproportionation of trimethyltin o-bromobenzoate occurred on heating. A quantitative study of this and other triorganotin ester pyrolyses would be of interest, but such an investigation lies outside the scope of our present interests.

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\(^3\) C. V. Wilson, Org. Reactions 9, 332 [1957].

\(^4\) R. Okawara and E. G. Rochow, J. Amer. chem. Soc. 82, 3285 [1960].