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STUDIES OF ORGANOMETALLIC COMPOUNDS
XXXIII. BROMINATION OF [2,3-BIS(ETHOXYCARBONYL)PROPYL]TRI-n-BUTYLTIN AND HYDROLYSES OF ITS MONOBROMINATION PRODUCT

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SUMMARY

[2,3-Bis(ethoxycarbonyl)propyl]-n-butyltin dibromide (III) was synthesized by the reaction between [2,3-bis(ethoxycarbonyl)propyl]tri-n-butyltin (I) and three equivalents of bromine in chloroform solution. It is believed that (III) contains a five-membered ring structure and has intramolecular interaction between the tin atom and the C=O at the δ-position with respect to the tin on the basis of IR spectrum.

[2,3-Bis(ethoxycarbonyl)propyl]di-n-butyltin bromide (II) was hydrolyzed. It was elucidated on the basis of elementary analysis, molecular weight data and IR spectrum, that the product of hydrolysis in hot aqueous alcoholic sodium hydroxide was a dimer with bridging structure.

INTRODUCTION

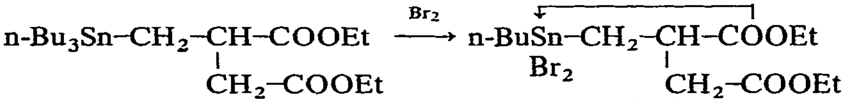
In previous papers[1,2] we have reported the syntheses of [2,3-bis(alkoxycarbonyl)propyl]tri-n-butyltin [$n\text{-Bu}_3\text{Sn–CH}_2\text{–CH(COOR)–CH}_2\text{–COOR}$ (I'), R = Me, Et (I), n-Pr, n-Bu] and [2,3-bis(alkoxycarbonyl)propyl]di-n-butyltin bromide [$n\text{-Bu}_2\text{SnBr–CH}_2\text{–CH(COOR)–CH}_2\text{–COOR}$ (II'), R = Me, Et (II), n-Pr] which contained a five-membered ring structure[1-6].

In this study dibromide (III) was easily prepared by adding an excess of bromine to (I). Compound (II) was hydrolyzed. The molecular structures of the products are of interest since intramolecular coordination of C=O groups to tin seems to occur.

DISCUSSION

Bromination of [2,3-bis(ethoxycarbonyl)propyl]tri-n-butyltin (I)

In previous papers[1,2] it was reported that compounds of type (II) were easily prepared at room temperature in high yields by adding the theoretical amounts of bromine to (I). (I) did not react completely with three equivalents of bromine even if the reaction mixtures were refluxed for several hours, and dibromide (III) was obtained.



$$n\text{-}Bu_3Sn{-}CH_2{-}\underset{\displaystyle CH_2{-}COOEt}{CH}{-}COOEt \xrightarrow{Br_2} n\text{-}Bu\underset{\displaystyle Br_2}{Sn}{-}CH_2{-}\underset{\displaystyle CH_2{-}COOEt}{CH}{-}COOEt$$

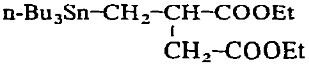
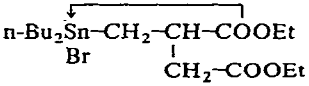
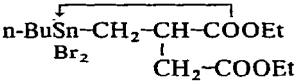
(I) (III)

The IR data comparing (I), (II) and (III) are shown in Table 1.

TABLE 1

THE C=O STRETCHING VIBRATIONS OF (I), (II) AND (III)

Positions of bands in cm^{-1}.

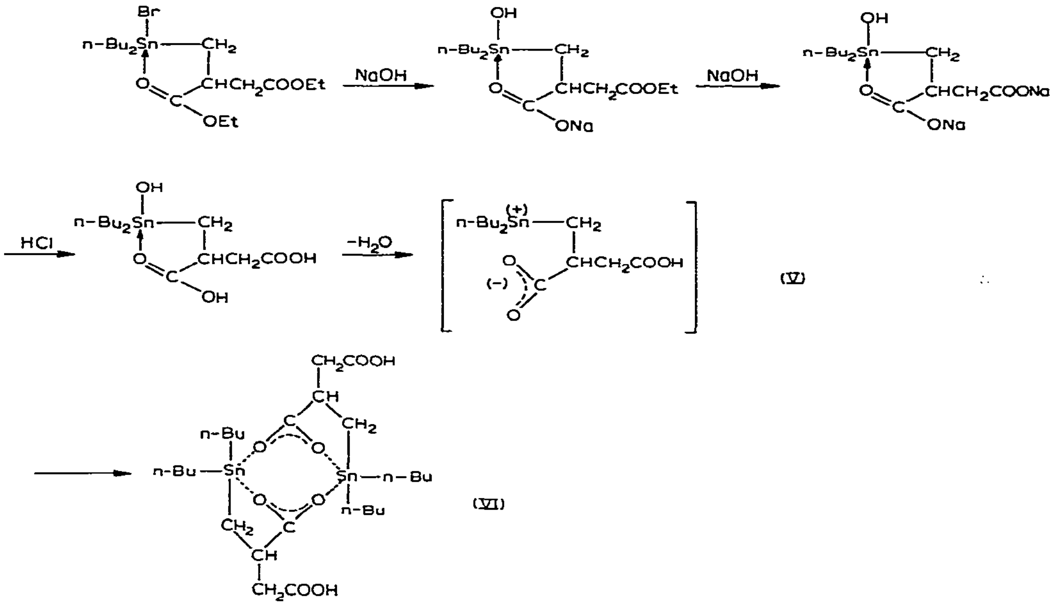
No.	Compound	γ(C=O) stretch		δ(C=O) stretch	
		Liq. film	In CCl_4	Liq. film	In CCl_4
(I)	 $n\text{-}Bu_3Sn{-}CH_2{-}\underset{\displaystyle CH_2{-}COOEt}{CH}{-}COOEt$	1736		1736	
(II)	 $n\text{-}Bu_2\underset{\displaystyle Br}{Sn}{-}CH_2{-}\underset{\displaystyle CH_2{-}COOEt}{CH}{-}COOEt$	1678	1685	1736	1735
(III)	 $n\text{-}Bu\underset{\displaystyle Br_2}{Sn}{-}CH_2{-}\underset{\displaystyle CH_2{-}COOEt}{CH}{-}COOEt$	1675	1681	1732 1704	1733

In the IR spectrum of (III) the absorption at 1675 cm^{-1} in liquid film and at 1681 cm^{-1} in carbon tetrachloride solution of (III) must result from the coordination of the oxygen atom of the C=O at the γ-position with respect to the tin [as in the case of (II)]. The other absorptions at 1732, 1704 cm^{-1} in liquid film of (III) were assigned to the C=O stretch of the ester group at the δ-position, which was observed only at 1733 cm^{-1} in solution. Hence, the absorption found at 1704 cm^{-1} was assigned to the C=O stretching frequency of the ester at the δ-position which was expected from the interaction of the other tin atom in liquid state. This intermolecular interaction must result because the tin becomes more electropositive in (III) than in (II) when bonded to two electronegative halogen atoms.

Base-catalyzed hydrolyses of (II)

Van der Kerk *et al.*[7,8] obtained an inner salt ($Ph_2\overset{+}{Sn}CH_2CH_2COO^-$) (IV) which was almost insoluble and infusible, from hydrolysis of (2-alkoxycarbonylethyl)-triphenyltin. But no inner salts were obtained from other (ω-alkoxycarbonylalkyl)-triphenyltin compounds. Hence they suggested that it depended greatly on the position of the carbonyl group with respect to the tin atom whether the free carboxylic acid is stable or whether an inner salt is formed. This kind of salt was obtained from the reaction between triphenyltin hydride and acrylic acid or hydrolyses of (2-alkoxycarbonylethyl)trialkyltin compounds, (2-alkoxycarbonylethyl)diphenyltin bromide and (2-alkoxycarbonylethyl)dialkyltin bromide. Moreover, such compounds were obtained from the oxidation of [o-(hydroxymethyl)phenyl]triphenyltin or (2-carboxyethyl)triphenyllead[10].

Formation of these salts must be associated closely with our five-membered ring structure at least in the transition state[11]. Then (II) must be hydrolyzed at 60–70° by the route shown below.



(V)

(VI)

The elementary analysis and molecular weight data of the product were in good agreement with this structure for (VI).

The IR spectrum data of the product show typical absorption of both aliphatic carboxylic acid[12] (broad band centered about at 3000 cm^{-1} and sharp peak at 1712 cm^{-1}) and of alkyltin carboxylates[13-19] (1547 and 1425 cm^{-1}). The carbonyl stretching frequencies at 1547 and 1425 cm^{-1} are in agreement with those reported by Okawara *et al.*[14] and Van der Kerk *et al.*[15]. This product must have a bridged structure (VI) because molecular weight data showed it to be the dimer of (V).

Also, the 1547 and 1425 cm^{-1} peaks show penta-coordination for tin atom. Such bridging structures have been reported not only concerning the other tin compounds[20-22] but also for other metal compounds (Tl[23], Rh[24], Mo[25], Al[26] and Ga[26]).

EXPERIMENTAL

The preparation of (I) and (II) used in these experiments has been described previously[1,2]. Molecular weight determinations were performed using a Mechrolab vapor pressure osomometer in *N,N*-dimethylformamide solution. IR spectra were run in liquid film and potassium bromide pellets using a Hitachi EPI-2G infrared spectrophotometer with grating optics.

Preparation of [2,3-bis(ethoxycarbonyl)propyl]-n-butyltin dibromide (III)

Bromine (20.2 g, 0.126 mole), was added dropwise with stirring to a solution of 20 g (0.042 mole) of (I) in 150 ml of chloroform kept at room temperature for 1½ h and then the solution was refluxed for 3 h. After removal of the solvent and butyl bromide at reduced pressure, the residue was distilled *in vacuo*, the fraction with b.p. 152–159°/0.003–0.001 mm being collected. The yield was 15.8 g (72%), n_D^{20} 1.5364. (Found: C, 29.25; H, 4.52; Sn, 22.26. $C_{13}H_{24}Br_2O_4Sn$ calcd.: C, 29.86; H, 4.63; Sn, 22.70%.)

Hydrolysis of [2,3-bis(ethoxycarbonyl)propyl]di-n-butyltin bromide (II)

A solution of 4 g (0.008 mole) of (II) in a solution of 0.9 g (0.025 mole) of sodium hydroxide in 40 ml of 75% ethanol was stirred at 60–70° for 2 h and the solution was kept at room temperature for two days. Then the solution was acidified with 1 *N* HCl (litmus paper) and was kept for a day. The solid which precipitated was filtered and washed several times with water and petroleum ether (1.7 g, 59% yield; m.p. 197–199°). This white solid was soluble in ethanol and *N,N*-dimethylformamide, insoluble in carbon tetrachloride, chloroform, benzene and dichloromethane. (Found: C, 42.71; H, 6.48; Sn, 32.84; mol. wt., 754. $C_{26}H_{48}O_8Sn_2$ calcd.: C, 43.01; H, 6.66; Sn, 32.70%; mol. wt., 726.)

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