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STUDIES OF ORGANOMETALLIC COMPOUNDS
XLIII. REACTIONS OF ORGANOTIN CHLORIDES WITH SODIUM AZIDE

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SUMMARY

Dialkyltin dichlorides R_2SnCl_2 ($R=CH_3$, C_2H_5, n-C_3H_7, and n-C_4H_9) react with sodium azide in the presence of water to give hexaalkyl-1,5-diazidotristannoxanes $N_3R_2Sn(OSnR_2)_2N_3$, tetraalkyl-1,3-dichlorodistannoxanes also give the same products. The configuration of the tristannoxane compound was established by X-ray diffraction study. On the other hand, dioctyltin dichloride yielded octaoctyl-1,7-diazidotetrastannoxane. Hexamethyl-1,5-diazidotristannoxane was treated with boiling methanol to give tetramethyl-1-azido-3-methoxydistannoxane, $N_3(CH_3)_2SnOSn(CH_3)_2OCH_3$.

INTRODUCTION

Only few organotin compounds have been reported in which azido groups are linked to tin atoms. All the organotin azides reported by 1966 were limited to trialkyl- or triaryltin compounds which were prepared by the reactions of trialkyl- or triaryltin chlorides with sodium azide in ether/water system[1]. In 1967, Lorberth *et al.*[2] obtained dialkyltin diazides $R_2Sn(N_3)_2$ ($R=CH_3$, C_2H_5, or n-C_4H_9) by the reaction between $R_2Sn(NR'_2)_2$ and HN_3 in an anhydrous system.

In 1953 Rochow *et al.*[3] reported that the reaction of dimethyltin dichloride and sodium azide gave what they believed to be a dimethyltin azide but the compound was not isolated. No other report on this reaction was found in the literature to date. While the authors intended to identify the products obtained by the reaction between organotin chlorides and sodium azide in methanol/water system, it was found that the products from lower R_2SnCl_2 were 1,5-diazidotristannoxanes, while that from dioctyltin dichloride was 1,7-diazidotetrastannoxane.

RESULTS AND DISCUSSION

The reactions of dialkyltin dichlorides (in which the alkyl groups were not longer than n-butyl) and sodium azide and water in methanol gave hexaalkyl-1,5-

diazidotristannoxanes, which also were obtained by using tetraalkyl-1,3-dichlorodistannoxanes instead of dialkyltin dichlorides.

$$\left.\begin{array}{l} R_2SnCl_2+NaN_3 \xrightarrow[\text{(eqn. 1)}]{H_2O} \\ ClR_2SnOSnR_2Cl+NaN_3 \xrightarrow[\text{(eqn. 2)}]{H_2O} \end{array}\right] \rightarrow N_3R_2Sn(OSnR_2)_2N_3$$

It is very interesting that dialkyltin dichlorides and tetraalkyldichlorodistannoxanes gave the same products. On the other hand, octaoctyl-1,7-diazidotetrastannoxane was obtained from dioctyltin dichloride by a similar reaction.

$$R_2SnCl_2+NaN_3 \xrightarrow{H_2O} N_3R_2Sn(OSnR_2)_3N_3 \qquad (3)$$

$$(R=n\text{-}C_8H_{17})$$

The tristannoxane compounds were identified by their IR spectra, elemental analyses and the fact that mixed melting points of both compounds prepared by eqn. (1) and eqn. (2) showed no depression. When an anhydrous methanol solution of sodium azide was mixed with a methanol solution of dialkyltin dichlorides or a tetrahydrofuran solution of tetraalkyl-1,3-dichlorodistannoxanes, precipitation of sodium chloride was not observed; the reaction was induced by the addition of water.

In the case of dioctyltin dichloride, when a methanol solution of dioctyltin dichloride was added to a methanol solution of sodium azide, white solid precipitated immediately. This white solid turned into oily liquid when the mixture was heated slightly; then water was added to give the tetrastannoxane compounds.

The authors cannot decide on a definitive reaction course in this paper, but the following scheme can be postulated, considering the above experimental results.

$$Na^+N_3^- + H_2O \rightleftarrows Na^+OH^- + HN_3 \qquad (4)$$

$$\left.\begin{array}{r} R_2SnCl_2 \\ ClR_2SnOSnR_2Cl \end{array}\right\} \xrightarrow[HN_3]{H_2O} XR_2Sn(OSnR_2)_nX' \qquad (5)$$

$$X, X'=N_3, OH, Cl;\ n \geqq 2$$

$$\xrightarrow{HN_3} N_3R_2Sn(OSnR_2)_nN_3 \quad n=2 \text{ or } 3 \qquad (6)$$

In the case of the compounds containing lower alkyl groups in eqn. (6), it was suggested that the tristannoxane structure ($n=2$) was the most stable, while in the n-octyltin compound the tetrastannoxane ($n=3$) was separated as the most stable compound.

It seems that the polystannoxane compounds in eqn. (5) correspond to oily products which are separated out during the reactions as described later; although these structures are not determined definitely in this paper.

The existence of a tristannoxane configuration has been proved by an X-ray diffraction study of the product prepared from dibutyltin dichloride and sodium azide. Although the crystal structure analysis was not fully successful in locating the light atoms because of the instability of the crystal and because of the very high

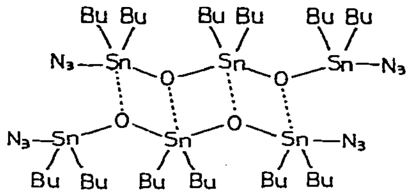

Fig. 1. Proposed structure of hexa-n-butyl-1,5-diazidotristannoxane by X-ray analysis.

content of tin atoms, a centrosymmetrical dimeric tristannoxane structure has been determined as shown in Fig. 1.

Hexamethyl-1,5-diazidotristannoxane was treated with refluxing methanol to give crystals of tetramethyl-1-azido-3-methoxydistannoxane.

EXPERIMENTAL

Starting materials

Dialkyltin dichlorides used in this paper were prepared by direct reaction methods from alkyl halides and tin foil[4]. Tetraalkyl-1,3-dichlorodistannoxanes were prepared by partial hydrolysis of dialkyltin dichlorides[5].

*Reactions of dialkyltin dichlorides or tetraalkyl-*1,3-*distannoxanes with sodium azide*

Sodium azide (10 g) was dissolved in 500 ml of methanol, then 100 ml of a methanol solution of dibutyltin dichloride (12 g) was added, followed by stirring for 20 min at room temperature. An oily liquid separated out on the wall of the flask after a dropwise addition of water (500 ml) with stirring. When further stirring was continued for 2 h at room temperature, white solid of hexamethyl-1,5-diazidotristannoxane was precipitated, with the evolution of a little hydrogen azide which had a characteristic odor. The yield was 7 g after recrystallization from benzene.

When tetraalkyl-1,3-dichlorodistannoxanes were used as starting materials, they were dissolved in 100 ml of tetrahydrofuran. A minor modification in the preparative procedure for the octyltin compound was described previously.

TABLE 1

PREPARATION OF DIAZIDO COMPOUNDS

Diazido compounds $N_3R_2Sn(OSnR_2)_nN_3$		Starting materials [g (mole)]			Yields [g (%)][a]	Recryst. solvent	M.p. (°C)
		R_2SnCl_2	$ClR_2SnOSnR_2Cl$	NaN_3			
$R=CH_3$	$n=2$	11 (0.05)		7.8 (0.12)	7 (75)	Methanol	>230
$R=C_2H_5$	$n=2$	10 (0.04)		6.5 (0.10)	6 (70)	Methanol	>230
$R=n\text{-}C_3H_7$	$n=2$	11 (0.04)		10 (0.15)	5 (51)	Benzene	207~210
			10 (0.02)	4 (0.06)	5 (51)		
$R=n\text{-}C_4H_9$	$n=2$	12 (0.04)		10 (0.15)	7 (64)	Benzene	173~175
			14 (0.025)	4 (0.06)	9 (65)		
$R=n\text{-}C_8H_{17}$	$n=3$	10 (0.024)		4 (0.06)	5 (56)	n-Hexane	96~ 98

[a] The yields were calculated from the following reactions: 3 mole of R_2SnCl_2 ($R=CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9$)→ 1 mole of tristannoxane; 3 mole of distannoxanes→2 mole of tristannoxanes or 4 mole of $(C_8H_{17})_2SnCl_2$→ 1 mole of tetrastannoxane.

The amounts of the reagents used in the similar reactions are shown in Table 1, and the melting points and elemental analyses of the diazido compounds obtained are summarized in Table 2.

TABLE 2

ANALYTICAL DATA OF DIAZIDO COMPOUNDS

Diazido compounds $N_3R_2Sn(OSnR_2)_nN_3$		Analyses, found (calcd.) (%) C	H	N	Sn	Mol.wt.[a]
$R=CH_3$	$n=2$	12.79	3.25	13.97	63.66	
		(12.81)	(3.23)	(14.95)	(63.32)	
$R=C_2H_5$	$n=2$	21.69	4.62	12.42	54.96	
		(22.29)	(4.68)	(13.00)	(55.08)	
$R=n\text{-}C_3H_7$[b]	$n=2$	29.62	6.11	11.39	49.29	763 (0.42)
		(29.56)	(5.79)	(11.50)	(48.73)	791 (0.78)
						(731)
$R=n\text{-}C_4H_9$[c]	$n=2$	35.42	6.88	10.20	43.62	818 (0.50)
		(35.38)	(6.68)	(10.31)	(43.70)	833 (1.20)
						(815)
$R=n\text{-}C_8H_{17}$	$n=3$	50.07	8.88	5.28	31.07	1575 (0.86)
		(50.82)	(9.06)	(5.56)	(31.39)	1552 (1.53)
						(1513)

[a] Determined by vapor pressure osmometry; concentration (% w/w) in parentheses. [b] Product obtained from distannoxane, found: C, 29.59; H, 5.86; N, 11.27; Sn, 48.49%. [c] Product obtained from distannoxane, found: C, 35.40; H, 6.71; N, 10.22; Sn, 44.03%.

Partial methanolysis of hexamethyl-1,5-diazidotristannoxane

Hexamethyl-1,5-diazidotristannoxane (7 g) was heated in 200 ml of boiling methanol for 5 h. Tetramethyl-1-azido-3-methoxydistannoxane (6 g, 83%) was obtained after recrystallization from methanol. (Found: C, 15.50; H, 3.93; N, 10.71; Sn, 61.45. $C_5H_{15}N_3O_2Sn_2$ calcd.: C, 15.53; H, 3.91; N, 10.87; Sn, 61.41%.) M.p. >230°. NMR (10% in benzene): τ 7.25 (s, 3 H, OCH_3); 9.40 (s, 6 H, $SnCH_3$) and 9.55 (s, 6 H, $SnCH_3$).

X-ray determination of the chemical structure of hexa-n-butyl-1,5-diazidotristannoxane

The crystals were recrystallized from a cyclohexane/benzene solution to form brittle, colorless needles developed along the *a* axis. Using Ni-filtered Cu-K_α radiation, the unit cell dimensions were determined from oscillation and Weissenberg photographs taken along the *a* and *b* axes.

Crystal data. $C_{24}H_{54}N_6O_2Sn_3$, $M=814.8$; triclinic; $a=9.72$, $b=14.49$, $c=15.80$ Å; $\alpha=120.9$, $\beta=76.2$, $\gamma=86.7°$; $U=1810$ Å^3; $Dm=1.49$ (by flotation); $Z=2$; $Dx=1.49$; $F(000)=406$.

Intensity data were collected by multiple-film equi-inclination Weissenberg photographs taken along the *a* axis (layers from 0 through 6), with Ni-filtered Cu-K_α radiation. As the crystal is unstable in air, it was sealed in a thin-walled glass capillary tube. However, after each exposure it was found necessary to renew the crystal by a freshly recrystallized one of approximately the same size. A total of only 874 independent reflections were obtained. The intensity data were corrected for

Lorentz and polarization effects in the usual manner. The inter-layer scale factors were made proportional to the exposure time of the X-ray.

The structure was established by the heavy atom method. Owing to the difficulties mentioned before, a complete structure analysis was not fully successful, however, a dimeric skeleton of the tristannoxane structure was obtained. Approximate coordinates of the tin atoms are given in Table 3.

TABLE 3

APPROXIMATE COORDINATES OF THE TIN ATOMS IN HEXABUTYL-1,5-DIAZIDOTRISTANNOXANE

	x	y	z
Sn(1)	0.153	−0.023	0.026
Sn(2)	0.181	−0.027	0.269
Sn(3)	0.134	−0.019	−0.218

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