ORGANOTIN CHEMISTRY

VIII*. THE REACTION OF DIBUTYLTIN OXIDE WITH *vic*-GLYCOLS

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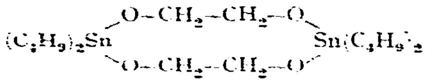
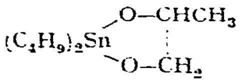
INTRODUCTION

The fact that diorganotin oxides react with vicinal glycols is known[3,**]. In particular, the disclosure of Ramsden and Banks[3] showed the reaction to be quite general. These authors, however, presented very little basis for the assignment of structures to the reaction products. Subsequently, it was proposed[1] that the reaction product of dibutyltin oxide and ethylene glycol was the ten-membered ring: 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (I). Also, even though no experimental detail was given, Bornstein *et al.*[4] agreed with the conclusion, advanced by Ramsden and Banks[3], that the reaction product of dibutyltin oxide and propylene glycol was 2,2-di-*n*-butyl-4-methyl-2-stanna-1,3-dioxolane (II).


(I)


(II)

This class of compounds suggested itself for further study for a number of reasons. First of all, they are remarkable for their resistance to hydrolysis. Even though they can be hydrolyzed[1], all of the compounds in this study are indifferent to adventitious moisture. This is in contrast to the hydrolytic lability of the organotin alkoxides[5] or phenoxides[6]. Furthermore the possibility of obtaining geometric isomers was intriguing. The ten-membered ring (I) is capable of supporting such isomerism if a substituted glycol is used. If the ten-membered ring was the rule in this series it was hoped that such isomers could be isolated.

EXPERIMENTAL

All m.p.'s are uncorrected. Molecular weights were determined on the Mechrolab Osmometer, Model 301 operated at 37.0°. Infrared spectra were run on the Beckman IR-8 and near-infrared on the Beckman DK-2 spectrophotometers.

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[*] For previous paper see ref. 1.
[**] See references in ref. 2.

Materials

Ethylene glycol was Baker's A.R. grade. *meso*-2,3-Butanediol was prepared from *trans*-2,3-epoxybutane (Farchan Labs) by the method of Wilson and Lucas[7]. Material used had b.p. 90°/20 mm (lit.[7] 89°/16 mm). *trans*-1,2-Cyclohexanediol (Aldrich Chemical) was recrystallized from acetone to a constant melting point. *cis*-1,2-Cyclohexanediol (Frinton Labs) was used as received.

1,1,6,6-Tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane

Dibutyltin oxide (125.0 g; 0.5 mole) and ethylene glycol (31.0 g, 0.5 mole) were added to 1250 ml of dry benzene contained in a three-neck flask equipped with a Dean and Stark moisture trap. During stirring, the contents of the flask were heated to and held at reflux (dibutyltin oxide dissolves) until a constant volume of 9.0 ml of liquid had collected in the trap. Vapor chromatographic analysis showed the liquid to be water (97.6 %) and ethylene glycol (1.1 %) with traces of benzene and "low boilers".

Upon cooling, the clear yellow-brown benzene solution deposited white crystals which were isolated by filtration, washed with benzene and dried in vacuum; yield 137.0 g (91 %). Recrystallization from benzene or methylene chloride did not change the melting point of 223–226.5° (lit.[4] 223–229). Exposure of the product to air, overnight, did not affect the melting point. (Found: C, 41.36, 41.21; H, 7.45, 7.35; Sn, 40.45; mol. wt. in $CHCl_3$, 650. $C_{20}H_{44}O_4Sn_2$ calcd.: C, 40.99; H, 7.57; Sn, 40.52 %; mol. wt., 586.) The infrared spectra in chloroform (ethanol-free) and carbon disulfide showed no hydroxyl absorption. Examination of the near infrared region confirmed the complete absence of hydroxyl.

trans-Di-n-butyltin-1,2-dioxycyclohexane

Dibutyltin oxide (107 g, 0.45 mole) and *trans*-1,2-cyclohexanediol (52.2 g, 0.45 mole) were reacted in 1 l of dry benzene as above. After a constant volume of 7.5 ml of water (theory 8.1 ml) had been collected in the trap the benzene was evaporated to give 137.0 g (96 %) of an almost white crystalline powder; m.p. 228–30°. After one recrystallization from benzene the melting point had reached a constant value of 234–6°. (Found: C, 48.78, 48.57; H, 8.10, 8.08; Sn, 34.36; mol. wt. in $CHCl_3$, 360. $C_{14}H_{28}SnO_2$ calcd.: C, 48.44; H, 8.07; Sn, 34.20 %; mol. wt., 347.) The infrared spectrum showed the absence of hydroxyl.

cis-Di-n-butyltin-1,2-dioxycyclohexane

Dibutyltin oxide (19.3 g, 77.5 mmole) and *cis*-1,2-cyclohexanediol (9.0 g, 77.5 mmole) were reacted with 170 ml of dry benzene as above. After a constant value of 1.4 ml of water (theory 1.4 ml) had been collected in the trap the benzene was evaporated to give 25.6 g (96 %) of white crystals; m.p. 162–3°. One recrystallization from benzene raised the melting point to a constant value of 164–5°. (Found: C, 48.79, 49.04; H, 8.30, 8.34; Sn, 34.06; mol. wt. in $CHCl_3$, 380. $C_{14}H_{28}SnO_2$ calcd.: C, 48.44; H, 8.07; Sn, 34.20%; mol. wt., 347.) The infrared spectra showed no hydroxyl.

2,2-Di-n-butyl-cis-4,5-dimethyl-2-stanna-1,3-dioxolane

Dibutyltin oxide (82.7 g, 0.33 mole) and *meso*-2,3-butanediol (30.0 g, 0.33 mole) were reacted in 500 ml of dry benzene as above. After a constant volume of 6.0 ml of water (theory 5.6 ml) had been collected in the trap the benzene was evaporated to give 104.2 g (98 %) of white crystals with a m.p. of 124–6°; unchanged by recrystallization from benzene. (Found: C, 45.00, 45.11; H, 8.27, 8.18; Sn, 37.01; mol. wt. in benzene, 330. $C_{12}H_{26}O_2Sn$ calcd.: C, 44.89; H, 8.16; Sn, 36.98 %; mol. wt., 321.) The infrared spectrum showed the absence of hydroxyl.

DISCUSSION

The reaction of dibutyltin oxide and ethylene glycol was restudied because Bornstein and his co-workers observed a weak band which could be attributed to O–H stretching in the infrared spectrum of the product; as run in chloroform. This observation would support a linear structure such as (III). Examination of the O–H region, in both the near- and middle-infrared region, and in a mull as well as in a variety of

$$HO{-}Sn(C_4H_9)_2OCH_2CH_2OSn(C_4H_9)_2OCH_2CH_2OH$$

(III)

solvents failed to turn up any suggestion of a band*, eliminating the linear structure. The results of the infrared and molecular weight studies support the ten-membered ring structure (I).

The reaction product of dibutyltin oxide and propylene glycol has been formulated[3,4] as the dioxolane (II) without any reported experimental basis. Because preliminary studies on this compound showed it to be too insoluble for osmometric molecular weights, attention was turned to more highly substituted glycols. The readily available *trans*-1,2-cyclohexanediol was studied first. The infrared spectrum again was blank in the O–H region. The molecular weight data show clearly that the dibutyltin derivative of this glycol has the five-membered ring structure. If dibutyltin oxide is considered to be a ketone analogue this result is surprising, since the acetone derivative of *trans*-1,2-cyclohexanediol does not form[8,]**.

Infrared spectra and molecular weights show that *cis*-1,2-cyclohexanediol also forms the 2-stanna-1,3-dioxolane – the five-membered ring. Since Emeléus and Zuckerman[10] have already reported that catechol also forms stanna-1,3-dioxolanes, it is apparent that the five-membered ring is quite common and insensitive to the stereochemistry of the starting glycol. This situation is not surprising, in retrospect. It is obvious that the larger size of the tin atom, in comparison to carbon (covalent radii[11]: C, 0.77 Å; Sn, 1.40 Å), will modify many of the stereochemical generalizations based upon experience with carbon compounds; yet, the instant series of compounds is the first available to illustrate this point.

To preclude the possibility that the formation of five-membered rings could be ascribed to the fused ring system arising from the use of *vic*-cyclohexanediols, the reaction of di-*n*-butyltin oxide with *meso*-butanediol-2,3 was investigated. Again, infrared and molecular weight evidence supports the five-membered 2-stanna-1,3-dioxolane structure. This gives credence to the structure (II) advanced by previous

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* It is possible that chloroform stabilized with ethanol was used by the previous workers.

** Recently, it has been shown by Brimacombe *et al.*[9] that *trans*-hexahydro-1,3-benzodioxolane can be formed from *trans*-1,2-cyclohexanediol and methylene chloride (or bromide) with sodium hydride.

workers for the product obtained with propylene glycol. It also indicates the five-membered ring to be the general case.

Recently, two conflicting reports of a very similar system have appeared. Pommier and Valade[12], in a very preliminary communication on the transalcoholation of dialkyltin dialkoxides with glycols, reported ring compounds are formed exclusively. These authors, however, report no experimental data and no clear idea of the structures obtained. Mehrotra and Gupta[13] report the reaction of dibutyltin diethoxide with glycols. They conclude that the products of their reaction exhibit varying tendencies to polymerize. Unfortunately, neither paper gives physical constants for their products so that a comparison is impossible.

The remaining question, perhaps the most interesting question, cannot be answered at present. Why does ethylene glycol give ten-membered rings while 2,3-butanediol and, presumably, propylene glycol give five-membered rings? The conformational analysis of large rings, and rings containing large atoms, has not progressed to the point where a meaningful analysis can be made.

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SUMMARY

Diorganotin oxides are known to react with *vic*-dihydroxy compounds. With catechol the product has been shown to be a 4,5-benzo-2-stanna-1,3-dioxolane while with ethylene glycol the 1,6-distanna-2,5,7,10-tetraoxacyclodecane is obtained. Only one other glycol, propylene glycol, had been investigated and the 5-membered dioxolane structure has been proposed without any experimental support.

The work reported is concerned with the reaction of dibutyltin oxide with a variety of aliphatic and alicyclic *vic*-glycols. All of the products are shown to have a 5-membered ring (with the exception of the product from ethylene glycol itself). The implication of these results for the stereochemistry of tin are considered.

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