PREPARATION AND PROPERTIES OF SOME ORGANOTIN COMPOUNDS

I. DIBUTYLTIN GLYCOLATES

R. C. MEHROTRA AND V. D. GUPTA
The Chemical Laboratories, University of Rajasthan, Jaipur (India)
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The alkoxides of tin(IV) and their derivatives with mono- and bidentate ligands (including β-diketones and glycols) have been studied recently in these laboratories[1]. In view of recent interest in the coordination chemistry of organotin compounds, the reactions between dibutyltin diethoxide with glycols have now been examined. All the derivatives are either new or have not been characterized previously.

A survey of the literature revealed only two references on similar derivatives. In a search for stabilizing agents[2] in polymerization process the reactions of dibutyltin dichloride with ethylene and propylene glycols were investigated. In another publication[3] the reaction of ethylene glycol with dibutyltin oxide was described. Emeléus and Zuckerman[4] described the preparation and properties of cyclic esters of dialkyltin(IV) by the reaction of dialkyltin dichloride with catechol and 2,2'-dihydroxybiphenyl. They found that use of a hydrogen chloride acceptor such as sodamide was necessary. The products were shown to be monomeric in pyridine by ebullioscopic measurements.

For the preparation of the starting material, dibutyltin diethoxide, the reaction of dibutyltin dichloride with ethanol was first attempted in the presence of anhydrous ammonia, a technique which has been applied successfully in the preparation of alkyl alkoxides of silicon[5] and germanium[6]. However, in this case although the reaction did appear to proceed slowly as indicated by the separation of ammonium chloride, the products on distillation, after filtration and subsequent drying, were found to contain varying amounts of chlorine. These results can be understood on the basis of preferential formation of Sn–N bonds, a behaviour which can be correlated with similar experience in the preparation of tin tetraalkoxides[7]. Dibutyltin diethoxide was successfully synthesized in 88 % yield by the reaction of the dichloride with sodium ethoxide in ethanol and benzene.

The dibutyltin diethoxide was found to interchange its ethoxide groups readily with glycols in the presence of benzene; the ethanol–benzene azeotrope could be fractionated out, and by determining the amount of ethanol collected, the progress of the reaction could be followed. A number of dibutyltin glycolates, derived from ethylene glycol, 1,2-propanediol, 1,3-propanediol, 3-chloro-1,2-propanediol, 1,3-, 1,4-, and 2,3-butanediols, 1,5-pentanediol, 1,6-hexanediol, hexylene glycol (2-methyl-2,4-pentanediol) and pinacol (2,3-dimethyl-2,3-butanediol), were synthesized by the following general reaction:

$$\mathrm{Bu_2Sn(OC_2H_5)_2} + \begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}\!\!>\!\mathrm{(CH_2)_n} \longrightarrow \mathrm{Bu_2Sn}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{(CH_2)_n} + 2\mathrm{C_2H_5OH}$$

TABLE 1

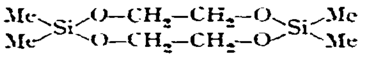
PROPERTIES OF DIBUTYLTIN GLYCOLATES

No.	*Parent glycol*	*Properties*	*Sublimation or distillation (°C/mm)*	*Molecular weight*			
				Solvent	*Total wt. of substance added (g/15 ml)*	*Found*	*Calcd.*
1	Ethylene glycol	Solid, crystallises from C_6H_6	Sublimed 220–240/0.3	Benzene Pyridine	0.651 0.746	964, 990, 948, 965 685, 640, 675	292.9 292.9
2	1,2-Propanediol	White solid, crystallises from C_6H_6	Sublimed 210–230/0.1	Benzene	0.478	740, 800, 832	307
3	1,3-Propanediol	White solid, crystallises from C_6H_6	184–185/0.3	Benzene Pyridine	0.919 0.639	560, 600, 540 520, 580, 530	307 307
4	1,3-Butanediol	Solid, crystallises from C_6H_6	105/0.25	Benzene	0.650	548, 543, 540, 547	321
5	1,4-Butanediol	Colourless highly viscous liquid	175–178/0.4	—	—	Molecular weight could not be determined due to the viscous nature of the product	
6	2,3-Butanediol	Solid, crystallises from C_6H_6	171–173/0.2	Benzene Pyridine	0.443 0.436	598, 630, 592, 580 580, 560, 570	321 321
7	3-Chloro-1,2-propanediol	White solid, crystallises from C_6H_6	Decomposes on distillation	—	—	—	—
8	1,5-Pentanediol	White solid, slightly soluble in C_6H_6	185–187°/0.15	—	—	—	—
9	1,6-Hexanediol	White solid	Decomposes on distillation	—	—	—	—
10	Hexylene glycol	Colourless viscous liquid	163–165/0.7–0.8	Benzene	0.766	580, 585, 570, 576	349
11	Pinacol	Low melting white solid	204–205/1.6	Benzene Pyridine	0.556 0.503	635, 617, 616, 640 475, 510, 518, 481	349 349

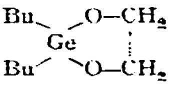
All the reactions were carried out in 1:1 molar ratio and were found to be quite facile. It should be mentioned that the corresponding reactions in the case of germanium require a catalyst except in the case of ethylene glycol[8]. Similarly, for the synthesis of some dimethylsilicon analogues[9,10] the use of a promoter such as *p*-toluenesulfonic acid is necessary.

The glycolate derivatives obtained were mostly as white solids or colourless viscous liquids, and could be sublimed or distilled *in vacuo* with the exception of the products of 3-chloro-1,2-propanediol and 1,6-hexanediol which appeared to undergo decomposition. They were all found to be soluble in common organic solvents like benzene, chloroform, and ether. The derivatives of hexylene glycol and pinacol were highly soluble in benzene whereas that of 1,6-hexanediol was found almost insoluble in benzene. They exhibit high thermal stability, but are readily hydrolyzed in solution.

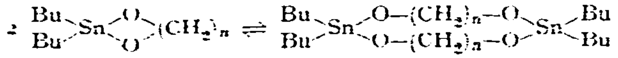
The data in Table 1 show that the glycolate derivatives exhibit varying tendencies to polymerization. The dimethylsilicon ethylene glycolate has been shown[9] to have the formula:



The corresponding dibutyl derivative in the case of germanium[8] has been found to be monomeric:



The molecular weight determinations suggest that equilibria of the following type are present in the case of tin derivatives:



The equilibrium appears to be shifted to the left to some extent in a donor solvent like pyridine.

EXPERIMENTAL

Apparatus and chemicals

Special precautions were taken for rigorous exclusion of moisture. Fractionations were carried out in a long column packed with Raschig rings and fitted to a total-condensation variable take-off stillhead.

Molecular weights were determined by a semimicro-ebulliometer (Gallenkamp) with thermistor sensing. Benzene was stored over sodium wire for two days, refluxed over sodium, and distilled. Finally it was dehydrated azeotropically with ethanol. Ethanol was dried over calcium oxide, followed by distillation over magnesium ethoxide. Finally it was fractionated with benzene. Ether was dried over sodium wire. Chloroform was refluxed with aluminium isopropoxide and distilled. Pyridine was

TABLE 2

PREPARATION AND ANALYSES OF DIBUTYLTIN GLYCOLATES

No.	$Bu_2Sn(OC_2H_5)_2$ (g)	Glycol (g)	Yield (%)	Ethanol		Analysis							
				Found (g)	Calcd. (g)	Found				Calcd.			
						C	H	Sn	Glycoxy	C	H	Sn	Glycoxy
1	3.68	Ethylene glycol (0.71)	98	0.94	1.04	...	...	40.4	19.9	...	—	40.5	20.4
2	3.36	1,2-Propanediol (0.79)	92	0.91	0.95	...		38.0	23.7	...	—	38.6	24.1
3	3.80	1,3-Propanediol (0.89)	78	0.90	1.08	42.4	7.90	38.7	...	43.0	7.87	38.6	—
4	2.5	1,3-Butanediol (0.68)	83	0.60	0.71	44.8	8.45	37.1	...	44.8	8.16	36.9	—
5	3.34	1,4-Butanediol (0.91)	78	0.80	0.95	44.5	8.64	36.7	...	44.8	8.16	36.9	—
6	2.76	2,3-Butanediol (0.75)	93	0.74	0.78	45.2	8.15	36.5	27.2	44.8	8.16	36.9	27.4
7	2.71	3-Chloro-1,2-propanediol (0.93)		0.74	0.77	38.00	6.77	35.0	...	38.0	6.78	34.7	—
8	4.09	1,5-Pentanediol (1.32)	72	1.00	1.16	40.53	8.60	35.0	...	40.6	8.42	35.4	—
9	3.2	1,6-Hexanediol (1.17)		0.84	0.91	48.06	8.8	34.2	...	48.1	8.66	34.0	—
10	3.53	Hexylene glycol (1.28)	77	0.93	1.0	49.0	9.01	34.0	...	48.1	8.66	34.0	—
11	2.75	Pinacol (1.00)	92	0.75	0.78	...	...	34.6	33.5	...	—	34.0	33.2

distilled from pellets of potassium hydroxide and then fractionated from aluminium isopropoxide. Dibutyltin dichloride of high purity was distilled under reduced pressure. Glycols were purified by distillation before the reaction.

Analytical methods

The compounds were decomposed by a mixture of fuming nitric acid and fuming sulphuric acid and weighing of the dehydrated oxide SnO_2. Ethanol in the azeotrope was determined by oxidation with chromic acid[11,12]. Glycols were estimated by oxidation with periodic acid[13]. Dichromate was used for pinacol. The determinations of carbon and hydrogen were carried out by Messrs. H. PIETERS and WIM BUIS, Microanalytical Department, University of Amsterdam.

(1) *Attempted preparation of dibutyltin diethoxide by the ammonia method*

A slow current of anhydrous ammonia (dried by passing through towers of aluminium isopropoxide) was passed into a mixture of dibutyltin dichloride (13.0 g), ethanol (19.0 g) and benzene (39.0 g). In the first half hour there was no change, but later crystalline ammonium chloride appeared, with very slight evolution of heat. The supply of ammonia was continued for about 10 h and the mixture was left overnight, and then filtered. The filtrate was refluxed to expel excess ammonia and then concentrated by distilling out excess of ethanol and benzene. The remaining solvent was evaporated to dryness under reduced pressure and the compound distilled. Three fractions, 5.1 g (103–109°/0.3–0.4 mm), 2.1 g (109–136°/0.4 mm) and 5.1 g (136–137°/0.4 mm), were collected. They contained chlorine in a varying amount.

(2) *Preparation of dibutyltin diethoxide by the sodium method*

To a refluxing solution of sodium ethoxide (sodium 6.7 g) in ethanol (42.0 g) was added dropwise dibutyltin dichloride (44.6 g) dissolved in benzene (68.0 g). Crystalline sodium chloride separated immediately. After the addition, refluxing was continued for 8 h, and the mixture was left overnight and filtered. Most of the ethanol and benzene were removed by normal distillation, and the remainder under reduced pressure. Distillation gave a colourless viscous liquid (42.0 g; yield 88 %). (Found: C, 43.92; H, 8.31; Sn, 36.8. $C_{12}H_{28}O_2Sn$ calcd.: C, 44.6; H, 8.73; Sn, 36.7 %.)

(3) *Reaction of dibutyltin diethoxide with glycols in a molar ratio of 1:1 in benzene*

To a benzene solution of dibutyltin diethoxide was added the calculated amount of glycol. The reaction mixture was refluxed at 110–115° and the ethanol produced was immediately fractionated as binary azeotrope and estimated. The remaining solvent was stripped off under reduced pressure at room temperature (30–35°/0.1–0.6 mm). The product was distilled under reduced pressure. The results of these experiments are given in Table 2.

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SUMMARY

The reactions of dibutyltin diethoxide with a number of glycols have led to the isolation of a number of new distillable dibutyltin glycolates. These products exhibit high thermal stability. Molecular weight determination showed them to be polymeric.

REFERENCES

1 V. D. Gupta, Ph.D. Thesis, Rajasthan University, Jaipur, 1965.
2 H. E. Ramsden and C. K. Banks, U.S. 2,789,994, April 23, 1957; *Chem. Abstr.*, 51 (1957) 14786.
3 J. Bornstein, B. R. La Liberté, T. M. Andrews and J. C. Montermoso, *J. Org. Chem.*, 24 (1959) 886.
4 H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.*, 1 (1964) 328.
5 R. C. Mehrotra and B. C. Pant, *J. Indian Chem. Soc.*, 39 (1962) 65.
6 R. C. Mehrotra, G. Chandra, A. K. Rai and S. Mathur, *J. Organometal. Chem.*, 4 (1965) in the press.
7 D. C. Bradley, E. V. Caldwell and W. Wardlaw, *J. Chem. Soc.*, (1957) 4775.
8 R. C. Mehrotra, G. Chandra, A. K. Rai and S. Mathur, *J. Organometal. Chem.*, 4 (1965) in the press.
9 R. H. Krieble and C. A. Burkhard, *J. Am. Chem. Soc.*, 69 (1947) 2689.
10 M. M. Sprung, *J. Org. Chem.*, 23 (1958) 58.
11 D. C. Bradley, F. M. A. Halim and W. Wardlaw, *J. Chem. Soc.*, (1950) 3450.
12 R. C. Mehrotra, *J. Indian Chem. Soc.*, 31 (1954) 904.
13 T. N. Misra, Ph.D. Thesis, Rajasthan University, Jaipur, 1963.

J. Organometal. Chem., 4 (1965) 145–150