UDC 547.841.89:547.258.11

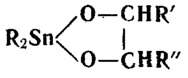
CYCLIC GLYCOL ETHERS DERIVED FROM DIALKYLSTANNANEDIOLS

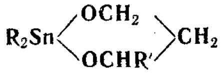
M. G. Voronkov and Yu. P. Romadan

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 6, pp. 892-896, 1966

The splitting of polydialkylstannoxanes $(R_2SnO)_m$ is studied by 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-glycols. In this way ten glycol ethers of dialkylstannanediols, mainly with 5, 6, or 10-membered rings, are obtained, eight of which were previously unknown.

As far back as 1952 the patent literature [1, 2] mentioned splitting of polydibutylstannoxane (dibutyltin oxide) with glycols. It was further shown that reaction of dibutyldichlorostannane with propane-1,2-diol and butane-1,3-diol give 2,2-dibutyl-4-methyl-2-stanna-1,3-dioxolane (Ia) and 2,2-dibutyl-4-methyl-2-stanna-1,3-dioxane (IIa) respectively:


I


II

a $R=n\text{-}C_4H_9$, $R'=CH_3$, $R''=H$;
b $R=C_2H_5$, $R'=CH_3$, $R''=H$;
c $R=C_2H_5$, $R'=R''=CH_3$;

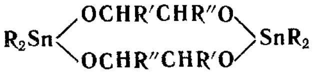
a $R=n\text{-}C_4H_9$, $R'=CH_3$;
b $R=C_2H_5$, $R'=H$.

At the same time, the product of reaction of dibutyldichlorostannane with ethylene glycol was wrongly assigned [3] a linear structure (III, R = n-Bu):

$$HOCH_2CH_2(OSnR_2OCH_2CH_2)_2OH$$

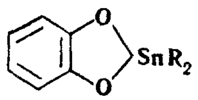
III

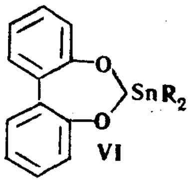
Contradicting this [3], it was later shown that [4] reaction of ethylene glycol both with dibutyldichlorostannane and with polybutylstannoxane gives 2,2,7,7-tetrabutyl-1,3,6,8-tetraoxa-2,7-distannacyclodecane (IVa).


IV

a $R=n\text{-}C_4H_9$, $R'=R''=H$;
b $R=C_2H_5$, $R'=R''=H$;
c $R=C_2H_5$, $R'=CH_3$, $R''=H$;
d $R=C_2H_5$, $R'=R''=CH_3$.

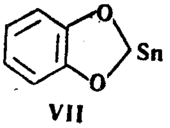
Reaction of dialkyldichlorostannanes with catechol and 2,2'-dihydroxydiphenyl [6] gives the corresponding cyclic ethers of dialkylstannediols, V and VI

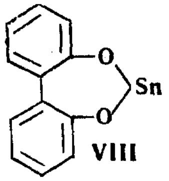

V


VI

$R=CH_3$; $n\text{-}C_4H_9$.

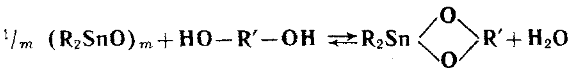
The action of catechol or 2,2'-dihydroxydiphenyl on copper-tin alloy gives, respectively, heterocyclic compounds VII and VIII [5]


VII

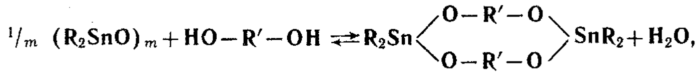

VIII

They are also obtained [6] by the action of stannous chloride on catechol or 2,2'-dihydroxydiphenyl in the presence of sodamide.

In the present paper a study is made of the splitting of polydialkylstannoxanes (dialkyltin oxides) by means of 1,3-, 1,3-, 1,4-, 1,5-, and 1,6- alkane diols.* Splitting of $[(C_2H_5)_2SnO]_m$ and $[(n\text{-}C_4H_9)_2SnO]_m$ by glycols proceeds mainly in accordance with the equation



or



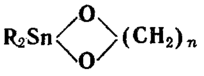
where R is a monovalent, and R' a divalent organic group.

With 1,2- and 1,3-glycols this reaction gives cyclic ethers of the corresponding dialkylstannanediols of type I, II, or IV, with 5, 6, or 10-membered rings. Thus reaction of $(R_2SnO)_m$ with ethylene glycol gives the dimeric compounds IVa and IVb, containing 10-membered heterocyclic rings.

Splitting of $[(C_2H_5)_2SnO]_m$ with propane-1,2-diol and butane-2,3-diol gives cyclic ethers which can be assigned the structures of, respectively, 2,2-diethyl-4-methyl-2-stanna-1,3-dioxane (Ib) and 2,2-diethyl-4,5-dimethyl-2-stanna-1,3-dioxolane (Ic), containing 5-membered rings. But the high sublimation temperatures and melting points of these compounds, which are close to that of IVb, make it possible to assume that they are both dimers with a structure, evidently similar to that of IV.

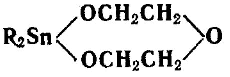
The reaction product from polydidethylstannoxane and propane-1,3-diol is 2,2-diethyl-2-stanna-1,3-dioxane (IIb).

The reaction of $(R_2SnO)_m$ with higher α,ω-alkanediols $HO(CH_2)_nOH$ (n = 4–6) also gives the corresponding ethers of dialkylstannanediols, and these might have been assigned structure IX:



IX

a $n=4$; b $n=5$;
c $n=6$



X

a $R=n\text{-}C_4H_9$;
b $R=C_2H_5$

However, the fact that these compounds do not melt above 150°–200° C suggests that they are not monomers.

At the same time, reaction of polydialkylstannoxanes with diethylene glycol gives monomeric 2,2-dialkyl-2-stanna-1,3,6-trioxacyclooctane (X) which readily distils under reduced pressure.

The table gives yields, physical constants and analyses of the compounds prepared. They are all crystalline, generally they sublime or distil at 10^{-3} or 10^{-4} mm, and are rather stable in moist air,** unlike their acyclic analogs, the alkoxystannanes [8].

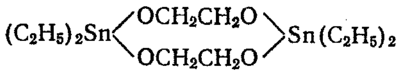
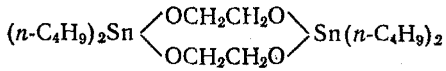
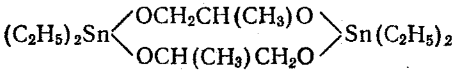
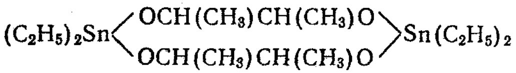
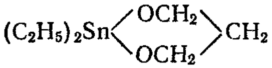
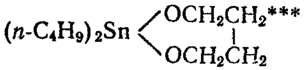
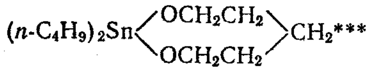
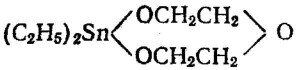
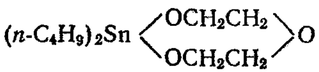
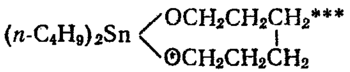
The low solubilities of most of the compounds prepared made it very difficult to determine their molecular weights. Still, from a number of results, it can be concluded that the sizes of the rings of the dialkylstannanediol ethers are determined by the same principles that operate with cyclic ethers of dialkylsilanediols [7]. However, quite apart from this, when considering the structure of cyclic ethers of dialkylstannanediols, it is impossible to exclude the possibility that their molecules associate, with involvement of the tin atom as electron-acceptor, and of the oxygen atoms as electron-donors. This problem, results for IR and PMR spectra, and other physical properties of cyclic ethers of dialkylstannanediols, making it possible to fix their structures unequivocally, will form the subject of a subsequent paper.

---

* We previously [7] described a similar reaction of glycols with polydialkylsiloxanes.

** E. g., many cyclic ethers of dialkylstannanediols can be kept for days exposed to air without their melting points changing.

Cyclic Glycol Ethers of Dialkylstannanediols

Comp. no.	Structural formula	Mp, (bp), °C	Molecular formula	Found, %			Calculated, %			Yield, %
				C	H	Sn	C	H	Sn	
IVb*	 $(C_2H_5)_2Sn\begin{smallmatrix}OCH_2CH_2O\\OCH_2CH_2O\end{smallmatrix}Sn(C_2H_5)_2$	280	$C_{12}H_{28}Sn_2O_4$	30.47 30.52	5.93 6.03	49.74 49.75	30.42	5.96	50.11	86
IVa**	 $(n\text{-}C_4H_9)_2Sn\begin{smallmatrix}OCH_2CH_2O\\OCH_2CH_2O\end{smallmatrix}Sn(n\text{-}C_4H_9)_2$	229.5—230	$C_{20}H_{44}Sn_2O_4$	40.88 41.57	7.57 7.54	39.92 40.04	41.00	7.57	40.51	86
IVc*	 $(C_2H_5)_2Sn\begin{smallmatrix}OCH_2CH(CH_3)O\\OCH(CH_3)CH_2O\end{smallmatrix}Sn(C_2H_5)_2$	255	$C_{14}H_{32}Sn_2O_4$	33.30 33.26	6.57 6.48	47.20 47.17	33.51	6.43	47.31	95
IVd*	 $(C_2H_5)_2Sn\begin{smallmatrix}OCH(CH_3)CH(CH_3)O\\OCH(CH_3)CH(CH_3)O\end{smallmatrix}Sn(C_2H_5)_2$	246	$C_{16}H_{36}Sn_2O_4$	35.97 36.38	6.83 6.89	44.47 44.25	36.27	6.85	44.80	87
IIb*	 $(C_2H_5)_2Sn\begin{smallmatrix}OCH_2\\OCH_2\end{smallmatrix}CH_2$	169—173	$C_7H_{16}SnO_2$	33.36 33.18	6.46 6.49	47.29 47.74	33.51	6.43	47.31	90
IXa*	 $(n\text{-}C_4H_9)_2Sn\begin{smallmatrix}OCH_2CH_2^{***}\\ \vert\\ OCH_2CH_2\end{smallmatrix}$	decomp 195	$C_{12}H_{26}SnO_2$			37.41 37.57	44.90	8.16	36.97	92
IXb*	 $(n\text{-}C_4H_9)_2Sn\begin{smallmatrix}OCH_2CH_2\\OCH_2CH_2\end{smallmatrix}CH_2^{***}$	decomp 174	$C_{13}H_{28}SnO_2$			35.33 35.52	44.60	8.43	35.42	89
Xb*	 $(C_2H_5)_2Sn\begin{smallmatrix}OCH_2CH_2\\OCH_2CH_2\end{smallmatrix}O$	75—77 106—107 (0.5mm)	$C_8H_{18}SnO_3$	35.09 34.73	6.62 6.38	42.15 42.63	34.20	6.49	42.25	87
Xa**	 $(n\text{-}C_4H_9)_2Sn\begin{smallmatrix}OCH_2CH_2\\OCH_2CH_2\end{smallmatrix}O$	35—47 145—147 (3mm)	$C_{12}H_{26}SnO_3$	42.66 43.11	8.00 7.76	34.86 34.65	42.77	7.78	35.22	76
IXc*	 $(n\text{-}C_4H_9)_2Sn\begin{smallmatrix}OCH_2CH_2CH_2^{***}\\ \vert\\ OCH_2CH_2CH_2\end{smallmatrix}$	decomp 48	$C_{14}H_{30}SnO_2$	48.49 48.53	8.71 8.72	34.12 34.71	48.17	8.66	34.00	93

---

*New compound

**The literature gives: IVa, mp 195°–200°C [1, 2]; mp 215°–218°C [3]; mp 223°–229°C [4]; Xa, mp 120°–130°C [1, 2].

***Possibly this compound is not a monomer.

Experimental

Purification and physical constants of the starting glycols were previously described [7]. Polydiethyl- and polydi-n-butylstanoxanes (from the firm of Dr. T. Schuchardt, Munich) were used without further purification. The solvents used (xylene, toluene, benzene, and petrol ether) were distilled over Na.

Syntheses

The glycol for reaction and $(R_2SnO)_m$ were put in a 0.5–1 *l* round-bottom flask fitted with a water trap and reflux condenser. 0.1 mole of each was used, and 200–500 ml of appropriate inert solvent (xylene, toluene, or benzene). The reaction mixture was heated in an oil-bath until water no longer collected in the trap (~3 hr). After 3 hr the polydialkylstannoxane had usually dissolved completely. The hot solution was filtered through a preheated No. 4 Schott filter, and then cooled slowly. Next day the crystals formed were filtered off with suction, and vacuum-dried. They were further purified by recrystallization, or subliming (distilling) under high vacuum.

This method of preparing cyclic ethers of dialkylstannanediols is illustrated by the following examples.

2,2,7,7-Tetra-n-butyl-1,3,6,8-tetraoxa-2,7-distannacyclodecane (IVa). 6.2 g (0.1 mole) ethylene glycol, 24.9 g (0.1 mole) $[(n\text{-}C_4H_9)_2SnO]_m$, and 100 ml xylene were vigorously refluxed together for 2 hr, the water formed being removed by this continuous axeotropic distillation. The hot solution was filtered, the crystals which separated out of the filtrate were filtered off, and washed on the filter with petrol ether, then vacuum-dried. Yield of IVa, mp 227°–229° C, 25.2 g (86%). After recrystallizing from dry xylene it had mp 229.5°–230° C.

2,2-Diethyl-2-stanna-1,3-dioxane (IIb). 19.2 g (0.1 mole) $[(C_2H_5)_2SnO]_m$, 7.7 g (0.1 mole) propane-1,3-diol, and 600 ml xylene were heated together until water no longer separated in the trap (3 hr). The solution was filtered hot and left overnight. The crystals of IIb which separated out were filtered off with suction, and vacuum-dried. Yield 13.5 g (90%), mp 166°–170° C. After recrystallizing from dry toluene it had mp 169°–173° C.

2,2-Diethyl-2-stanna-1,3,6-trioxacycloctane (Xa). 19.2 g (0.1 mole) $[(C_2H_5)_2SnO]_m$, 10.6 g (0.1 mole) diethylene glycol, and 300 ml xylene were heated together as described above, for 2 hr. All the xylene was then distilled off, the residue vacuum-distilled to give 24.8 g (87%) Xa, bp 106°–107° C (0.5 mm). After distillation the compound crystallized in the receiver, mp 75°–77° C.

REFERENCES

1. S. L. Burt, U.S. Patent no. 2583084, 1952; C. A., **47**, 146, 1953.
2. Bacelite Corp., British Patent no. 664133, 1952; C. A., **46**, 11230, 1952.
3. H. E. Ramsden and C. K Banks, U.S. Patent no. 2789994, 1957; C. A., **51**, 14786, 1957.
4. J. Bornstein, B. R. LaLiberte, T. M. Andrews, and J. C. Montermaso, J. Org. Chem., 24, 886, 1959.
5. J. J. Zuckerman, J. Chem. Soc., 1322, 1963.
6. H. J. Emelèus and J. J. Zuckerman, J. Organomet. Chem., **1**, 328, 1964.
7. M. G. Voronkov and Yu. P. Romadan, KhGS [Chemistry of Heterocyclic Compounds], 879, 1966.
8. D. L. Alleston and A. G. Davies, J. Chem. Soc., 2050, 1962.

12 February 1965

Institute of Organic Synthesis
AS Latvian SSR, Riga