Synthesis and ^{1}H NMR study of some organotin derivatives of diethanolamines

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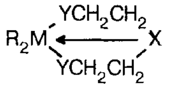
A number of organotin derivatives of diethanolamines (stannocanes) $R_2Sn(OCH_2CH_2)_2NR'$, $O(SiMe_2CH_2)_2Sn(OCH_2CH_2)_2NR'$, and $Sn[(OCH_2CH_2)_2NR']_2$ (R = Ph, *cyclo*-Hex; R′ = H, Me, Ph) were synthesized and studied by ^{1}H NMR spectroscopy. The effect of steric factors on the ability of molecules of stannocanes to form associates in solutions is discussed.

Key words: organotin compounds, stannocanes, synthesis, NMR, steric factors, associates.

Organometallic derivatives of diethanolamines and their *O*- and *S*-analogs have attracted increasing interest in recent years.

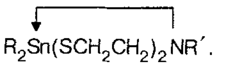


M = Si, Ge, Sn; Y = O, S; X = O, S, NR′.

Like other compounds with medium (7—10-membered) rings, they possess higher inner energy than the corresponding acyclic compounds.[1] This is mostly due to steric 1,4-interactions, torsion strains, and intramolecular nonvalent repulsions of opposite groups of atoms, which are compelled to be spaced at distances less than the sum of their Van der Waals radii («intramolecular crowding»). In addition, compounds with medium rings may occur as a great number of different conformers (for example, more than 10 conformers exist for cyclooctane). However, the differences in energy between the conformers are insignificant, which results in high conformational lability of medium rings in solutions. For eight-membered rings conformations close to the standard forms of cyclooctane, BB, CC, BC, and crown (C), are the most common.

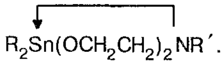
A general feature of type $R_2M(YCH_2CH_2)_2X$ eight-membered heterocycles containing M and X groups of atoms with pronounced acceptor and donor properties is the frequently occurring coordination 1,5-interaction.[1] For cyclic molecules containing Group IVB elements (Si, Ge, Sn), this interaction decreases the number of populated conformers; however, their number still causes complications in investigating the structure of these compounds in solutions. The M · · · X transannular distance may vary from the length of a strong covalent bond to that of a weak coordination bond having an electrostatic character and comparable with Van der Waals interaction. For derivatives of diethanolamine, the problem has long been debated whether the exchange of substituents at the M atom involves only pentacoordinate forms (occuring, for example, through the Berry rotation) or also tetracoordinate forms (occuring by a dissociative mechanism).[2—6] The authors of Ref. 7 have concluded that the exchange occurs *via* an open form whose lifetime is short.

The transannular interaction involving tin and nitrogen atoms has been most comprehensively studied[2—7] for stannocanes of the general formula



$R_2Sn(SCH_2CH_2)_2NR'$.

Unlike thio derivatives, oxygen-containing heterocycles[2—8] are prone to self-association both in solutions and in crystals due to the formation of a Sn←O intermolecular bond, which substantially complicates the investigation of the structure of stannocanes



$R_2Sn(OCH_2CH_2)_2NR'$.

Therefore, of the oxygen-containing stannocanes, only those which have bulky *tert*-butyl substituents at the tin atom have been examined by X-ray diffraction analysis and NMR.[4,7,8] The exchange processes exhibited in NMR spectra occur by a dissociation-inversion mechanism, and at low temperatures signals for two nonequivalent *tert*-butyl groups can be observed.[2,7]

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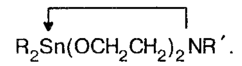
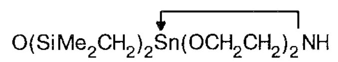
In the case of small substituents at the tin atom in the molecules



$$R_2Sn(OCH_2CH_2)_2NR'.$$

broadening of ^{1}H NMR resonance signals occurs, however, no good explanation of this phenomenon has been offered.

Previously[9] we explained the broadening of ^{1}H NMR signals in the resonance region of protons of the eight-membered heterocycle

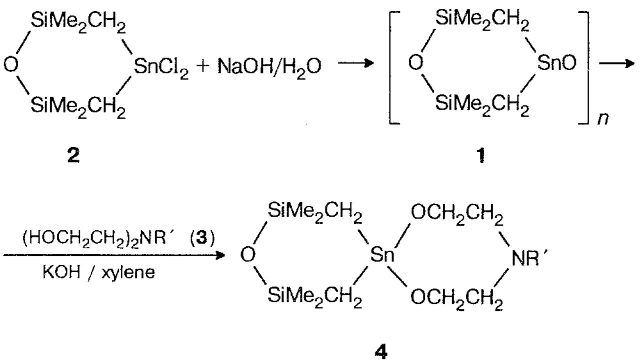


$$O(SiMe_2CH_2)_2Sn(OCH_2CH_2)_2NH$$

by reversible dissociation of the Sn←:N transannular bond. In the present work, to obtain more accurate information on this process, we prepared new oxygen-containing stannocanes and studied their ^{1}H NMR spectra.

Results and Discussion

In the present work we synthesized novel representatives of spirostannocanes **4** from heterocyclic oxide **1**, prepared from 1,1-dichloro-1-stanna-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane (**2**)[10], and diethanolamines **3** (method **A**).



R′ = H(**a**), Me(**b**), Ph(**c**).

The same stannocanes **4** were prepared from heterocyclic dichloride **2** and bis(tributylstannoxyethyl)amine **5** (method **B**):[9]

$$\mathbf{2} + \underset{\mathbf{5}}{(Bu_3SnOCH_2CH_2)_2NR'} \xrightarrow{\Delta} \mathbf{4} + Bu_3SnCl\,.$$

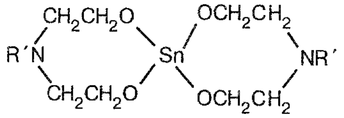
Dicyclohexylstannocanes **7** were synthesized in a similar way according to method **A** *via* the corresponding oxide **6**.

$$\underset{\mathbf{6}}{(cyclo\text{-Hex})_2SnO} + \underset{\mathbf{3}}{(HOCH_2CH_2)_2NR'} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{7}}{(cyclo\text{-Hex})_2Sn(OCH_2CH_2)_2NR'},$$

R′ = H(**a**), Me(**b**), Ph(**c**) .

Attempts to prepare diphenylstannocanes $Ph_2Sn(OCH_2CH_2)_2NR'$ (**8** R′ = Me(**a**), Ph(**b**)) by this method unexpectedly resulted in the formation of tetraphenylstannane and the corresponding spirodistannocanes, 4,12-diaza-1,7,9,15-tetraoxa-8-stannospiro[7,7]pentadecanes (**9**).



9

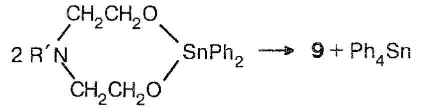
Such spirodistannocane structures were prepared from $Sn(OPr^i)_4$ and diethanolamine[12] or from $SnCl_4$ and an excess of triethanolamine.[13] It may be assumed that under these conditions (110—120 °C, KOH) the formation of Ph_4Sn and spirodistannocanes **9** occurs according to Schemes 1—3.

Scheme 1

$$2\,Ph_2SnO \longrightarrow Ph_4Sn + SnO_2$$

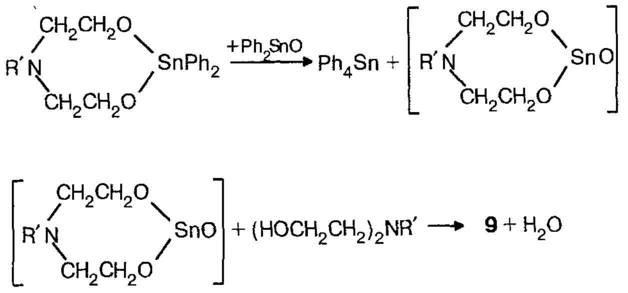
$$SnO_2 + 2\,(HOCH_2CH_2)_2NR' \longrightarrow \mathbf{9} + 2\,H_2O$$

Scheme 2



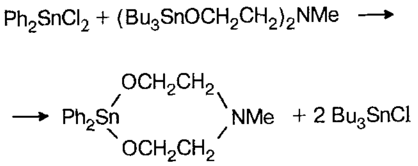
The fact that Ph_4Sn and spirodistannocanes are really formed according to Schemes 1—3 needs appropriate verification. At the same time, the individual steps of these schemes have analogies in the literature. For example, the formation of Ph_4Sn and SnO_2 according to Scheme 1 is supported by the fact that Me_4Sn has been detected among the products of thermal decomposition of Me_2SnO, along with ethane, stannic oxide, and stannous oxide.[14] Diphenylstannane oxide is likely to undergo disproportionation more readily than dimethylstannane oxide: we found that diphenylstannane oxide in boiling toluene for 1 h affords, according to GLC (a 1 m column, 5 % SE-30 on Chromaton N-AW-DMCS, temperature 180 °C, the rate of the carrier gas (helium) 60 mL min^{-1}) up to 7.3 % Ph_4Sn. We did not manage to confirm the second step of Scheme 1, the formation of spirodistannocanes **9**: diethanolamines did

Scheme 3



not undergo a reaction with an authentic sample of SnO_2. However, this does not mean that SnO_2 arising *in situ* also would not react with diethanolamines **3**.

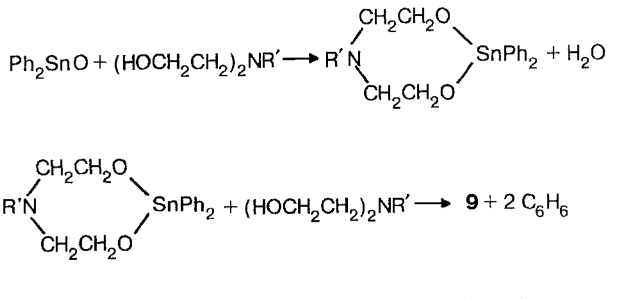
Disproportionation of diphenylstannocanes **8** according to Scheme 2 seems unlikely, since in the preparation of diphenylstannocane **8a** (R′ = Me) according to method **B** no spirodistannocane **9a** (R′ = Me) was detected among the reaction products.



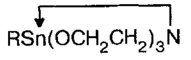
8 (yield 35 %)

The process according to method **A** may be more complex and may involve formation of spirodistannocanes **9**, for example, according to Scheme 4, in addition to the schemes under consideration.

Scheme 4



One piece of indirect evidence supporting the occurrence of the second step of this scheme is that alkylstannatranes

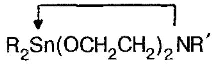


$RSn(OCH_2CH_2)_3N$

are formed in high yields (85—99 %) from $(R_2SnO)_n$ (R = Me, Et, Bu^n) and triethanolamine under similar conditions.[15]

The resulting organotin derivatives of diethanolamines (**4**, **7**, **8**, and **9**) are crystalline solids melting over rather narrow temperature intervals. Compound **4b** (R′ = Me) is distillable *in vacuo*. Yields, properties, and the data of elemental analysis for the compounds obtained are listed in Table 1 and the ^1H NMR spectroscopic data are summarized in Table 2.

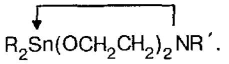
Molecules of stannocanes



$R_2Sn(OCH_2CH_2)_2NR'$

with relatively bulky[16] cyclohexyl (R = *cyclo*-Hex, $E^0_s = -1.19$) or *tert*-butyl (R = Bu^t, $E^0_s = -2.14$) substituents are not associated in a solution at R′ = Me, Ph (the signals for OCH_2 and NCH_2 methylene protons are not broadened). The substantial broadening of these signals for cyclohexylstannocane (R′ = H) results from the low rate of the dissociation-inversion process owing to the stronger Sn←N bond. In this case the ^1H NMR spectral lines become narrower as the temperature of the solution is increased, *i.e.*, the exchange process accelerates.

The fact that the transannular bond becomes stronger in the following order of R′: Ph < Me < H is supported by the known data from X-ray structural study of analogous silicon-containing derivatives of diethanolamines[17]



$R_2Sn(OCH_2CH_2)_2NR'$.

The Si←N bond length decreases in the following R′ order: Ph (3.08 Å), Me (2.68 Å), and H (2.30 Å). The shorter M←N contact for R′ = H in comparison with that for R′ = Me is due to the lower steric hindrance. The increase in the length of the transannular contact for R′ = Ph can be explained by substantial conjugation of the lone electron pair of the nitrogen atom with the aromatic system of the benzene ring.

The accepting ability of the tin atom in solutions of spirostannocanes **4** with small-sized $O(SiMe_2CH_2)_2$ substituents (E^0_s is approximately −0.5—0.6) is equal to that in cyclohexyl analogs **7**, and the donor ability of the nitrogen atom is also the same. Therefore, the considerable broadening of the ^1H NMR signals may be explained by intermolecular association of spirostannocanes **4** in solutions, which is confirmed by the narrowing of the signals of the methylene protons in the OCH_2 and NCH_2 groups at high temperatures due to a decrease in the extent of intermolecular association.

For symmetrical spirodistannocanes **9a,b** (R′ = Me, Ph) broadening of the signals of the methylene protons is not observed, which indicates that their molecules are not associated in solutions. This is explained by the fact that hexacoordination of the Sn atom in these molecules is provided by two Sn←N intramolecular coordination

Table 1. Yields, properties, and the elemental analysis data for compounds **4**, **7—9**

Compound	R′	Yield (%) Preparation method	M.p./°C [B.p./°C] (p/Torr)	Found/Calculated (%) C	H	Ash
4a	H	15.1 (A)	130—134	31.60	6.50	65.08
		58.3 (B)*		31.43	6.59	65.59
4b	Me	88.0 (A)	55—60	33.72	6.64	67.12
		84.5 (B)	[122—124/1]	33.35	6.87	68.36
4c	Ph	78.6 (A)	Decomposes at	41.75	6.95	58.71
		89.5 (B)	$T > 120$°C	41.95	6.38	59.10
7a	H	80.0 (A)	184—185	50.22	8.04	37.52
				49.50	8.05	38.82
7b	Me	81.0 (A)	85—87	49.98	8.70	37.24
				50.77	8.27	37.47
7c	Ph	74.0 (A)	170—175	56.85	7.33	32.51
		53.0 (B)		56.92	7.60	32.46
8	Me	35.0 (B)	209—220	51.96	5.05	39.01
			(dec)	52.35	5.43	38.63
9a	Me	65.6 (A)	185—190	34.98	6.03	42.33
			(dec)	34.03	6.28	42.69
9b	Ph	49.6 (A)	Decomposes at	50.40	5.12	31.64
			$T > 250$°C	50.35	5.49	31.58

* The yield of compound **4**[11] prepared by method **B** was 40 %, m.p. 110—112 °C

Table 2. Parameters of the ^{1}H NMR spectra of compounds **4**, **7—9**

Compound	R	Solvent	T/°C	δ OCH$_3$	NCH$_2$	Other
4a	H	CHCl$_3$	25	3.85[a]	2.90[a]	0.18(SiMe); 0.21(Sn—CH$_2$)
		C$_6$H$_5$NO$_2$	150	3.93	2.92	0.22(SiMe); 0.35(Sn—CH$_2$)
4b	Me	CHCl$_3$	25	3.71[a]	2.62[a]	0.09(SiMe); 0.04(Sn—CH$_2$); 2.30(N—Me)
		C$_6$H$_5$NO$_2$	100	3.82	2.65	0.13(SiMe); 0.23(Sn—CH$_2$); 2.33(N—Me)
4c	Ph	CDCl$_3$	25	3.44[a]	3.69[a]	0.23(SiMe); 0.29(Sn—CH$_2$);7.39-6.63(N—Ph)
		C$_6$H$_5$NO$_2$	150	3.99	3.50	0.08(SiMe); 0.23(Sn—CH$_2$)[b]
7a	H	CHCl$_3$	60	3.78	2.80[a]	2.02—1.28(*cyclo*-Hex)
7b	Me	CDCl$_3$	25	3.54	2.49	1.70—1.40(*cyclo*-Hex); 2.20(N—Me)
7c	Ph	CDCl$_3$	25	4.06	3.43	1.70—1.26(*cyclo*-Hex); 7.37-6.80(N—Ph)
8	Me	CHCl$_3$	25	3.86[a]	2.83[a]	7.67—7.13(Sn—Ph); 2.09(N—Me)
9a	Me	CHCl$_3$	25	3.62	2.57	2.28(N—Me)
9b	Ph	CDCl$_3$	25	3.86	3.57	7.37—6.63(N—Ph)

[a] The signal is considerably broadened..

[b] Signals of the solvent are superimposed on the signals of aromatic protons.

bonds. The energy of the Sn←N transannular interaction is likely to be higher (due to the chelate effect) than that of intermolecular association in solutions occurring through the Sn←O coordination bond.

Experimental

All of the reactions were carried out under dry purified nitrogen. 1,1-Dichloro-1-stanna-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane (**2**) and the corresponding oxide **1** were prepared by the known procedures.[10] Dicyclohexyldichlorostannane (m.p. 88—89 °C) and diphenyldichlorostannane (m.p. 42—44 °C) were prepared from tetracyclohexylstannane and tetraphenylstannane, respectively, by a redistribution reaction with stannic chloride.[18]

^{1}H NMR spectra were recorded on a Tesla BS 467 spectrometer (operating at 60 MHz), tetramethylsilane was used as the internal standard.

Preparation of stannocanes 4, 7, 8, and 9

Method A. The corresponding diorganostannane oxide (0.02 mol) and diethanolamine (0.02 mol) were placed in a round-bottom flask (0.35 L) equipped with a stirrer, a thermometer, and a Dean and Stark distillation head. 250 mL of toluene (or xylene) and several crystals of KOH were added, and the mixture was stirred at 110—120 °C until the separation of azeotropic water was completed. Then the reaction mixture was cooled, the unreacted oxide was filtered off, and the solvent was evaporated *in vacuo*. The resulting precipitate of a stannocane was washed with hexane, dried *in vacuo* (30—40 °C (3 Torr)), and weighed. Spirostannocane 4 (R′ = Me) was distilled from a Claisen flask in a vacuum at 122—124 °C (1 Torr).

Reaction of diphenylstannane oxide with *N*-methyldiethanolamine

1.71 g (58.9 %) of tetraphenylstannane was isolated by filtration from the reaction mixture obtained from 5.35 g (0.0185 mol) of diphenylstannane oxide and 2.2 g (0.0185 mol) of *N*-methyldiethanolamine by method **A** after partial evaporation of the solvent and cooling to ~20 °C; m.p. 223—225 °C (from xylene). Literature data:[19] m.p. 225.7 °C. Found (%): C, 67.32; H, 4.77; Sn, 27.83. $C_{24}H_{20}Sn$. Calculated (%): C, 67.49; H, 4.72; Sn, 27.79. Extraction of the residue, obtained after evaporation of the solvent from the filtrate, with hexane afforded 2.1 g (yield 65.6 %) of spirodistannocane **9a** (R′ = Me) as a white powder. Spirodistannocane **9b** (R′ = Ph) was obtained from diphenylstannane oxide and *N*-phenyldiethanolamine in a similar way.

Method B. Diorganodichlorostannane (0.01 mol) and 60 mL of dry benzene were placed in a round-bottom flask (0.25 L) equipped with a stirrer, a dropping funnel, and a reflux condenser. A solution of 6.83 g (0.01 mol) of bis(2-tributylstannoxyethyl)amine in 80 mL of dry ether was added dropwise with stirring at 22—23 °C. The reaction mixture was stirred for an additional 1 h, and the precipitate was filtered off, washed with pentane, and dried. If no precipitate appeared during stirring, the solvent was evaporated *in vacuo*, and then the precipitate was also washed with pentane, dried *in vacuo* at 30—40 °C (3 Torr), and weighed.

Yields, properties, and the data of elemental analysis of the compounds synthesized are listed in Table 1 and ^{1}H NMR spectral data are given in Table 2.

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