

INTRAMOLECULAR MOBILITY OF PENTACOORDINATED TIN COMPOUNDS

C. MÜGGE, K. JURKSCHAT, A. TZSCHACH and A. ZSCHUNKE

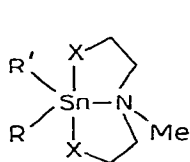
Department of Chemistry, Martin-Luther-University Halle-Wittenberg (G.D.R.)

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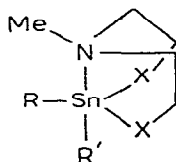
Summary

The ^1H and ^{13}C NMR data for some *N*-methyl-5,5-dialkyldiptychthiazastannolidines are reported. The differing coupling constants of the proton signals of the two nonequivalent Sn-alkyl groups suggest apical/equatorial positions for these groups at the pentacoordinated tin atom. The observed intramolecular process is explained by a dissociation-inversion mechanism.

In previous papers [1,2] we proposed a structure for *N*-alkyl-5,5-di-*t*-butyl-diptychoxazastannolidines in which there is an approximate bipyramidal arrangement of the ligands around the tin atom. The electronegative oxygen atoms must lie in the apical positions [3], and the *t*-butyl group and N atoms in equatorial positions (structure A, X = O). The temperature dependence of the ^1H , ^{13}C and ^{119}Sn spectra of that compound is explicable in terms of a dissociation-inversion mechanism [1,2,4]. An alternative structure B (X = S) must be



(A)



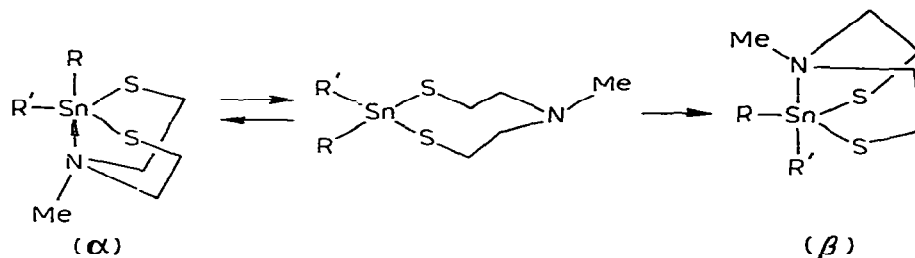
(B)

considered in the case of *N*-methyl-5,5-dialkyldiptychthiazastannolidines I–III (I, X = S, R = R' = Me; II, X = S, R = R' = *t*-Bu; III, X = S, R = Me, R' = *t*-Bu).

The ^1H NMR spectrum (see Table 1) of I at -20°C displays two Sn-methyl signals (a and b) of equal intensity but only one N-methyl signal. At $+41^\circ\text{C}$ the two Sn-methyl signals coalesce. In the ^1H NMR spectrum of II the two *t*-Bu signals (a and b) coalesce at -49°C . The ^1H NMR spectrum of III shows no temperature dependence.

The ^{13}C NMR spectra exhibit similar behaviour (see Table 2). At low temperature in the spectra of I and II only the ^{13}C signals of the Sn-alkyl groups are split, the SCH_2 , NCH_2 and NCH_3 signals remaining unchanged.

For reasons previously discussed a dissociation-inversion suggested to be the process whereby both methyl groups in I (or *t*-butyl groups in II) become equivalent.



For I and II both conformers (α and β) are equivalent; for III, however, one conformer dominates to such a degree that only one signal appears for each Sn-alkyl group even at low temperature.

In the *N*-alkyl-5,5-di-*t*-butyldiptychoxaazstannolidines the two Sn-alkyl signals, which appear at low temperature have almost the same coupling-constants $^3J(^{119}\text{Sn}-\text{C}-\text{C}-^1\text{H})$ and $^3J(^{117}\text{Sn}-\text{C}-\text{C}-^1\text{H})$. The ^1H NMR spectrum of II, however, gives a different value for the coupling constants $^3J(^{119}\text{Sn}-\text{C}-\text{C}-^1\text{H})$ and $^3J(^{117}\text{Sn}-\text{C}-\text{C}-^1\text{H})$ for both Sn-alkyl signals (see Table 3). The coupling constants $^2J(^{119}\text{Sn}-\text{C}-^1\text{H})$, $^2J(^{117}\text{Sn}-\text{C}-^1\text{H})$, $^1J(^{119}\text{Sn}-^{13}\text{C})$ and $^1J(^{117}\text{Sn}-^{13}\text{C})$ of the two methyl signals in I also differ considerably. Signal a: $^1J(^{119}\text{Sn}-^{13}\text{C})$ 472.2 Hz, $^1J(^{117}\text{Sn}-^{13}\text{C})$ 452 Hz; signal b: $^1J(^{119}\text{Sn}-^{13}\text{C})$ 341 Hz, $^1J(^{117}\text{Sn}-^{13}\text{C})$ 326 Hz at -20°C , solvent: CDCl_3 .

TABLE 1

 ^1H NMR CHEMICAL SHIFTS δ (ppm) OF I, II AND III

Compound	Sn-CH ₃		Sn-C-CH ₃		N-CH ₃	Temperature (°C)	Solvent
	(a)	(b)	(a)	(b)			
I	0.65	0.02			2.13	-70	CH_2Cl_2
	0.66	0.06			2.16	-26	CH_2Cl_2
	0.71	0.20			2.21	-10	CDCl_3
		0.47			2.25	+60	CDCl_3
	0.29	-0.37			1.83	-26	$(\text{CD}_3)_2\text{CO}$
	0.62	0.25			2.05	-3	<i>o</i> -DCB ^a
		0.5			2.10	+97	<i>o</i> -DCB
II			1.21	1.13	2.16	-72	CH_2Cl_2
				1.30	2.20	+34	CH_2Cl_2
			0.97	0.89	1.94	-72	$(\text{CD}_3)_2\text{CO}$
				1.13	2.11	+34	$(\text{CD}_3)_2\text{CO}$
III	0.55			0.93	2.16	-60	CH_2Cl_2
	0.62			1.04	2.20	+34	CH_2Cl_2

^a *o*-DCB = *o*-dichlorobenzene, conc. ca. 1 M.

TABLE 2

 ^{13}C NMR CHEMICAL SHIFTS δ (ppm) OF I, II AND III

Com- pound	Sn-CH ₃		Sn-C-CH ₃	Sn-C-CH ₃	S-CH ₂	N-CH ₂	N-CH ₃	Tempera- ture (°C)
	(a)	(b)						
I	4.4	2.7			23.7	58.4	42.7	-20
		2.5			23.7	58.4	42.7	+40
II			30.1	37.4	23.1	59.1	41.2	-30
III	-2.6		28.9	33.3	23.4	58.5	43.0	+40

^a Solvent-CDCl₃, conc. ca. 1 M.

These facts suggest apical/equatorial positions for the Sn-alkyl groups at the pentacoordinated tin atom (see structure B).

The small difference between the electronegativities of sulfur and carbon would favour similar stabilities for structures A and B. Because these two structures never appear as conformers in the low-temperature spectrum we believe the partial Berry process [5,6] between A and B to be fast on the NMR time scale even at the lowest accessible temperatures. In I, II and III structure B must dominate in the equilibrium. An alternative explanation, involving an intermediate structure between A and B, cannot be excluded [7].

The difference in the free activation enthalpies for I and II demonstrates that in comparison with the methyl group the *t*-butyl group weakens the Sn-N bond, both electronic and steric factors being responsible for this.

Experimental

All reactions were carried out under dry oxygen-free argon. The solvents were purified by standard methods. *N*-Methyl-bis(β -mercaptoethylamine) was made as previously described [8].

The *N*-methyl-5,5-dialkyldiptychthiazastannolidines was prepared by a method as previously described for the *N*-alkyl-5,5-dialkyldiptychthiazastannolidines [1,2]. The ¹H NMR spectra (100 MHz) were recorded on a Varian-HA-100 spectrometer; proton-decoupled ¹³C NMR spectra were recorded on a Bruker HX-90E spectrometer.

N-Methyl-5,5-dimethyldiptychthiazastannolidine (I). Dimethyltin oxide (5.8 g 0.035 mol), *N*-methyl-bis(β -mercaptoethylamine) (0.035 mol, 5.28 g) and a catalytic amount of potassium hydroxide in 125 ml of xylene yield, after recrystallisation from benzene/*n*-pentane, 9.85 g (94%) of *N*-methyl-5,5-dimethyldiptychthiazastannolidine (m.p. 66°C). (Anal.: Found: C, 28.14; H, 5.77; N, 4.62; Sn, 39.51. C₁₇H₁₇NS₂Sn calcd.: C, 28.22; H, 5.71; N, 4.70; Sn, 39.87%).

N-Methyl-5,5-di-*t*-butyldiptychthiazastannolidine (II). Di-*t*-butyltin oxide (10 g, 0.04 mol), *N*-methyl-bis- β -mercaptoethylamine (6.079, 0.04 mol), and a catalytic amount of potassium hydroxide in 150 ml of xylene gave, after evaporation of the solvent and distillation, 14.5 g (94.5%) of *N*-methyl-5,5-di-*t*-butyldiptychthiazastannolidine (b.p. 152°C/0.8 mmHg; m.p. 38°C). (Anal.: Found: C,

TABLE 3
 PROTON COUPLING CONSTANTS J (Hz) FOR I, II AND III

Compound	$^2J(^{113}\text{Sn}-\text{C}-^1\text{H})$		$^2J(^{117}\text{Sn}-\text{C}-^1\text{H})$		$^3J(^{112}\text{Sn}-\text{C}-\text{C}-^1\text{H})$		$^3J(^{117}\text{Sn}-\text{C}-\text{C}-^1\text{H})$		Temperature (°C)	Solvent
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)		
I	64	49	61	45					-26	CH_2Cl_2
	64	49	61	45					-26	CDCl_3
	64	48.5	61	46					-26	$(\text{CD}_3)_2\text{CO}$
	64	48.5	61	46					-26	Pyr.- d_5
	64	48.5	61	46					-26	<i>o</i> -DCB ^a
II		56.5		54					+97	<i>o</i> -DCB
					101	91	97	87	-72	CH_2Cl_2
					90		86		+34	CH_2Cl_2
					100	89	96	85	-72	$(\text{CD}_3)_2\text{CO}$
					89		85		+34	$(\text{CD}_3)_2\text{CO}$
III	52		50		88		84		-60	CH_2Cl_2
	52		50		86		84		+34	CH_2Cl_2
	52		50		87.5		83.5		+34	DMSO
	52.5		50		88		84		+34	Pyr.- d_5

^a *o*-DCB = *o*-dichlorobenzene, conc.: ca. 1 *M*.

TABLE 4
ACTIVATION PARAMETERS ^a (kJ/mol) OF I AND II

Compound	T _c (°C)	G [*] _{T_c}	H [*]	E _a	Solvent
I	41.0	65.3	61.1 (± 4.0)	63.2 (± 4.0)	CDCl ₃
	40.5	65.7	64.0 (± 2.0)	66.5 (± 2.0)	Pyr.-d ₅
II	-49.4	48.5	44.8 (± 4.5)	46.9 (± 4.5)	CH ₂ Cl ₂
	-49.5	48.5	56.5 (± 10.5)	58.2 (± 10.5)	(CD ₃) ₂ CO

^a T_c coalescence temperature; G^{*} free activation enthalpie; H^{*} activation enthalpie; E_a Arrhenius activation energy.

40.81; H, 17.72; N, 3.60; Sn, 30.92. C₁₃H₂₉NS₂Sn calcd.: C, 40.87; H, 17.60; N, 3.66; Sn, 31.10%).

N-Methyl-5-methyl-5-*t*-butyldiptychthiaazstannolidine (III). Methyl-*t*-butyltin oxide (3.7 g, 0.0179 mol), *N*-methyl-bis(β-mercaptoethylamine) (2.7g, 0.0179 mol), and a catalytic amount of potassium hydroxide in 100 ml of xylene gave after recrystallisation from benzene/pentane, 5.5 g (90.5%) of *N*-methyl-5-methyl-5-*t*-butyldiptychthiaazstannolidine, m.p. 94–95° C. (Anal.: Found: C, 35.32; H, 6.55; N, 4.07; Sn, 34.75. C₁₀H₂₃NS₂Sn calcd.: C, 35.32; H, 6.77; N, 4.12; Sn, 34.94%).

All the products are soluble in common organic solvents such as benzene, chloroform, acetone, and pyridine.

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