Journal of Organometallic Chemistry, 139 (1977) 279—282

INTRAMOLECULAR MOBILITY OF PENTACOORDINATED TIN COMPOUNDS

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

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

M.F. LARIN, V.A. PESTUNOVICH and M.G. VORONKOV

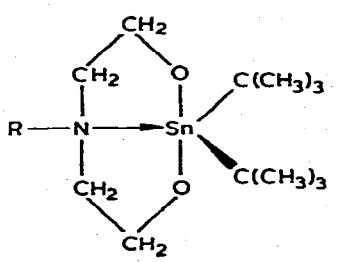
Institute of Organic Chemistry, Siberian Division of the Academy of Sciences of the U.S.S.R., Irkutsk (U.S.S.R.)

(Received May 16th, 1977)

Summary

The ^{119}Sn NMR and ^{13}C NMR data are reported for *N*-alkyl-5,5-di-t-butyldiptychoxazstannolidines. The activation parameters of an intramolecular process are estimated from the temperature dependence of the ^{1}H NMR spectra in different polar solvents. The NMR data support the dissociation—inversion mechanism for this process.

We propose for *N*-alkyl-5,5-di-t-butyldiptychoxazstannolidines I—V a structure which has nearly a trigonal bipyramidal arrangement of the ligands around the tin atom [1]. However a small distortion of the bonding towards a square pyramid (with oxygen at the top) is possible [2]. The temperature dependence of the ^{1}H NMR spectra provides a method of investigating the intramolecular exchange of these ligands. At 32°C the signal of the t-butyl protons is a singlet with ^{119}Sn and ^{117}Sn satellites. At low temperatures the signal turns into two signals of equal intensity. The process which makes both groups equivalent can be an intramolecular exchange of groups by Berry-pseudorotation [3] or by turnstile-rotation [4].



(I, R = H; II, R = Me; III, R = n-Bu; IV, R = i-Bu; V, R = t-Bu)

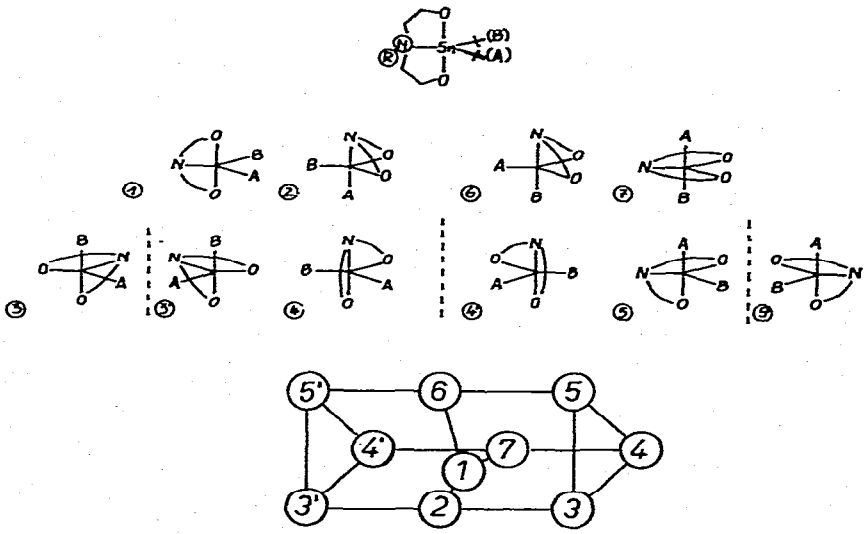


Fig. 1. Possible structure of *N*-alkyl-5,5-di-t-butyldiptychoxazstannolidines and a graph of these structures, related by Berry-pseudorotation.

Figure 1 shows, that an intramolecular exchange of the two t-butyl groups A and B by Berry-pseudorotation passes through the isomeric forms 6-5-3-2 or 7-4-3-2. Both pathways include structures of very high energy (ring-strain, steric hindrance). Similar consideration of the turnstile-rotation leads to the same result. Thus these processes are of low probability.

We propose instead a dissociation—inversion mechanism [1]. While the tin–nitrogen bond is broken the substituent at nitrogen changes its position by nitrogen inversion. This mechanism is supported by the estimation of the ^{119}Sn-chemical shifts by means of the heteronuclear double resonance (INDOR technique).

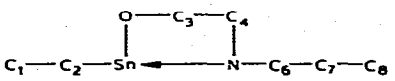
The ^{119}Sn-chemical shifts for I and II (Table 1) differ from those of the n-$Bu_2Sn(OEt)_2$ spectrum [5] by about 50 ppm. These results may probably be attributed to the effect of the replacement of two n-butyl radicals by two t-butyl groups in these molecules, rather than to a change in the coordination number of their Sn atoms. Indeed, the same difference in nuclear shieldings is observed for n-Bu_2SnCl_2 ($\delta(^{119}Sn)$ 122 ppm) and t-Bu_2SnCl_2 ($\delta(^{119}Sn)$ 52 ppm) [6]. Since n-$Bu_2Sn(OEt)_2$ (which is dimeric in solution [5]) is 5-coordinate I and II must

TABLE 1

^{119}Sn NMR CHEMICAL SHIFTS δ (ppm) (reference: $Sn(CH_3)_4$, positive sign at low field shift.)

Compound	Solvent CH_2Cl_2	Solvent $(CD_3)_2CO$	Temperature (°C)	Solvent CH_2Cl_2	Solvent $(CD_3)_2CO$	Temperature (°C)
I	−209.5	−210.5	+32	−214	−213	−40
				−213	−215	−40
II	−205	−204	+32	−207	−207	−40
				−207	−207	−40

TABLE 2

^{13}C NMR-CHEMICAL SHIFTS δ(ppm) IN 

(Reference: TMS, positive sign at low field shift)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
I	30.4	37.5	60.3	51.7				
II	30.4	37.7	62.0	57.5	39.5			
III	30.6	39.0	57.5	56.1	46.4	22.5	20.6	13.7
IV	30.5	38.2	57.5	56.4	54.2	23.3	20.6	
V	30.3	38.2	66.7	53.5	55.3	26.8		

also be 5-coordinate. However, the existence of the spin coupling between ^{119}Sn and ^{1}H nuclei in the Sn←N—CH_3 fragment of II [1] and a weak dependence of the Sn-chemical shifts upon the solvent in I and II excludes an association process for these molecules. Therefore the pentacoordination of Sn atoms in these molecules must come from intramolecular Sn···N bonds. At low temperatures two signals of the t-butyl groups appear in ^{1}H NMR spectra of I and II. However, monitoring the ^{119}Sn satellites of both lines in each proton spectrum gives us the same ^{119}Sn-chemical shifts in ^{1}H—{^{119}Sn} INDOR spectra for species I and II as well. That is, the ^{119}Sn signals resulting from molecules of the same kind and the nonequivalence of t-butyl protons are not caused by different conformers of I and II, but are due to the anisochronism of these groups in their sole conformer 1 (Fig. 1).

The chemical shifts of the ^{13}C signals (Table 2) of the nuclei C(3) and C(4) in compound III in comparison to compound IV show a steric compression shift caused by the t-butyl group. Table 3 shows the solvent dependence of the activation parameters: free activation enthalpy ΔG_c^* at the coalescence temperature T_c, activation enthalpy ΔH^* and Arrhenius' activation energy E_a of the compounds I and II. These parameters are estimated by measurement of the temperature dependent line-shape of the t-butyl-proton signals using approximative equations and total line-shape analysis [8].

In comparison with the ΔG^* values, the ΔH^* and E_a values are considerably greater. This can be explained by the easier conformational mobility of the eight-membered ring and thus the lower degree of regularity of the transition state. In the $CDCl_3$ solution of compound I this effect is apparently lost because of the formation of a N—H···N-hydrogen bond in the transition state.

TABLE 3

ACTIVATION PARAMETERS IN DIFFERENT SOLVENTS (kcal/mol) (error $\Delta G_c^* \pm 1$ kcal/mol, error ΔH^* and $E_a \pm 3$ kcal/mol)

Compound	ΔG_c^*	T_c(K)	ΔH^*	E_a	Solvent
I	15.2	284	11.6	12.2	$CDCl_3$
	15.9	297	22.6	23.2	$(CD_3)_2CO$
II	14.9	283	20.9	21.6	$CDCl_3$
	15.0	286	21.9	22.5	$(CD_3)_2CO$

Experimental

The NMR data listed in Table 1 were obtained by the $^{1}H-\{^{119}Sn\}$-INDOR method using a Tesla BS-487C (80 MHz for ^{1}H) spectrometer fitted with a universal device for heteronuclear double resonance [7].

The ^{13}C NMR spectra (Table 2) were recorded at 22.63 MHz with broad-band-proton decoupling on a Bruker HFX-90 R spectrometer. The *N*-alkyl-5,5-di-t-butyldiptychoxazstannolidines were synthesized by the same method [1].

References

1 A. Zschunke, A. Tzschach and K. Jurkschat, J. Organometal. Chem. 112 (1976) 273.
2 E.L. Muetterties and L.J. Guggenberger, J. Amer. Chem. Soc., 96 (1974) 1748.
3 R.S. Berry, J. Chem. Phys., 32 (1960) 933.
4 P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E.A. Tsolis and I. Ugi, Angew. Chem., 83 (1971) 691.
5 P.J. Smith, R.F.M. White and L. Smith, J. Organometal. Chem., 40 (1972) 341.
6 J.D. Kennedy and W. McFarlane, Rev. Silicon, Germanium, Tin and Lead Compounds, 1 (1974) 235.
7 M.F. Larin and V.A. Pestunovich, NMR Technical and Application Bulletin, Tesla Brno, No. 9 (1976) p. 1—7.
8 G. Binsch. J. Amer. Chem. Soc., 91 (1969) 1304.