Intermolecular Exchange and Configurational Stability of Organotin Alkoxides and Phenoxides

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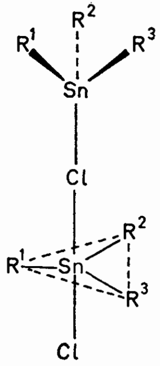
Chemical shift non-equivalence for the diastereotopic methyl groups of methyl-(2-methyl-2-phenylpropyl)phenyltin alkoxides and phenoxide is observed in benzene solution. Peak separation and line-width analysis show that in these compounds intermolecular exchange of OR groups (R = alkyl or phenyl) and configuration inversion at the tin atom proceed at a different rate, exchange being much faster than inversion. The change in bulk of the alkoxy-group, or its substitution with a phenoxy-group, brings about appreciable changes in the exchange rate but only marginally affects inversion. A mechanism involving intermolecular association and non-dissociative positional exchange of the groups bonded to tin is suggested. Addition of free alcohols or phenol shows that, while exchange of OR groups occurs between the tin derivative and these added compounds, the inversion rate is increased and this accounts for a different mechanism including transetherification. Experiments with alcohols or phenol containing an OR group different from that contained in the tin derivative support this point. Coalescence of diastereotopic methyls on adding dimethyl sulphoxide is observed only in the case of the organotin phenoxide. The role of steric and electronic effects of the R group is discussed.

ASYMMETRICALLY substituted organotin halides show in their n.m.r. spectra [1-4] coalescence of diastereotopic groups as a function of concentration, solvent polarity, and temperature. A ready intermolecular halogen exchange between two or more molecules of organotin halide and configurational inversion at the tin atom [2,3] would appear to be the reason for this. According to Stynes and Allred,[3] halogen exchange and inversion of configuration occur at the same rate through an associative mechanism which implies one of the two possible intermediates (1) or (2). Intermolecular exchange of OR groups has been observed in organotin alkoxides.[5-7] In compounds of general formula Bu_3SnOR the rate of exchange of the OR group depends on the nature of the R group and follows the order MeO > EtO > $PhCH_2O$ > Me_3CCH_2O. This information has been acquired [7] by studying the behaviour of the long-range coupling constant $J(^{117/119}Sn-O-C-H)$. In the case of the methoxy-derivative it was found that the approximate exchange rate of this group is higher than 80 s^{-1}, while lower values are to be attributed to larger groups. To explain the exchange of alkoxy-groups in these compounds an associative mechanism was suggested [6] through an intermediate of type (3). When a halogen atom and an alkoxy-group are present in the same molecule only oxygen bridges seem [7] to be present.



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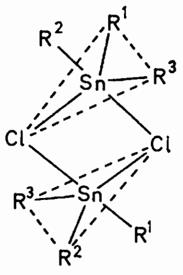

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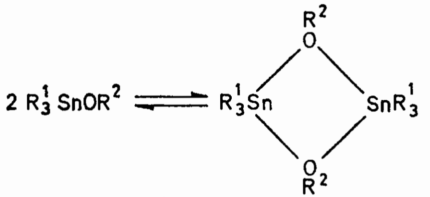

(3)

Exchange of NH_2 and NR_2 groups have also been

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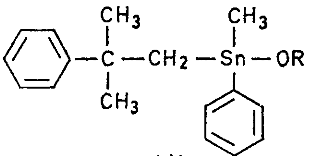
observed[8] in stannylamines, and the rate of exchange is strictly connected with the size of the R group on nitrogen and to that of groups directly bonded to tin. The problem of inversion at the tin atom in organotin alkoxides does not seem to have been tackled in previous studies, especially not in connection with intermolecular exchange of alkoxy-groups. The aim of this paper is to examine this exchange for a series of organotin alkoxides under several experimental conditions to observe if configurational inversion also occurs at the tin atom and to what extent the two phenomena are interdependent. The phenoxy-derivative is also taken into account in order to compare the behaviour of the phenyl with that of the alkyl groups.

RESULTS AND DISCUSSION

Compounds (4) were examined in the present work. The neophyl (2-methyl-2-phenylpropyl) group contains two diastereotopic[9] methyl groups which should, in principle, show chemical shift non-equivalence. As recently discussed by Peddle and Redl[2] for the halogen derivatives, in compounds (4) the two methyl groups of the neophyl group should be anisochronous in the absence of inversion of configuration at the tin atom, *i.e.* in the absence of exchange of their magnetic environments, and the magnitude of the chemical shift non-equivalence will depend upon the extent of the difference between their magnetic environments. A time-averaged signal should be observed when rapid exchange of the environments occurs. Apart from the exchange process, the extent of chemical shift non-equivalence should also depend on the relative rotamer populations around the bonds connecting the diastereotopic nuclei to the asymmetric centre.



(4)

a; R = Me
b; R = Pr^i
c; R = Bu^t
d; R = Ph

TABLE 1

Chemical shifts (p.p.m. from tetramethylsilane) and long-range coupling constants between tin and proton for compounds (4) measured in 0·5M-benzene solution

Compd.	δ_{CH_3} [a]	$\Delta\nu$/Hz [b]	δ_{CH_2}	$\delta_{CH_3(\alpha)}$	δ_{OR}	$J^{117/119}$Sn–H/Hz
(4a)	1·32	4·5	1·75	0·05	3·73	J[Sn–CH$_3$(α)] 54·1/56·4
(4b)	1·38	3·9	1·82	0·11	1·28 (CH$_3$) 3·98 (CH)	J[Sn–CH$_3$(α)] 54·7/57·1 J(Sn–O–CH) 37·5
(4c)	1·32	3·8	1·78	0·12	1·26	J(Sn–CH$_3$) 54·2/57·0
(4d)	1·26	4·1	1·92	0·11		J(Sn–CH$_3$(α)] 56·2/58·3

[a] Mean value for the two non-equivalent methyl groups.
[b] Internal shift between non-equivalent methyl groups.

The ^{1}H n.m.r. spectra of compounds (4) have been recorded in benzene solution at different concentrations. Some representative resonances are reported in Table 1. Broad signals are usually observed for all the protons when the compounds are analysed as pure liquids and we believe that this should depend on the high viscosity of the samples. A small amount of benzene gives sharp resonances and the diastereotopic groups show separate signals for all the derivatives examined. In Figure 1 the high-field part of the spectrum of compound (4a) is shown and refers to a 3M-benzene solution. No $^{117/119}$Sn satellite is observed for the OMe group and this could indicate[7] that the intermolecular exchange rate for this group should be >80 s^{-1}. An approximate estimate of the rate of inversion of configuration can be obtained from the separation of the resonances of diastereotopic methyl groups. The largest separation $\Delta\nu$ observed for these groups is 4·5 Hz, in dilute benzene solution, and from the approximate expression (1)[10,11]

$$p = \pi \, . \, \Delta\nu/\sqrt{2} \qquad (1)$$

a rate of inversion p *ca.* 10 s^{-1} relative to the coalescence point can be evaluated. Since coalescence is never reached for compounds (4) in benzene solution, the inversion rate should always be lower than 10 s^{-1}. A further check of this estimate can be made from comparison of the line-width of the diastereotopic methyl groups with that of the methyl group directly bonded to the tin atom; while the former tends to become broader as the concentration increases, the latter is sharp at any concentration in benzene solution. This observation is consistent with different inversion rates at the tin atom when the sample concentration is changed. For a *ca.* 1·5M solution of compound (4a) in benzene the difference in half-height band width of these two methyl groups is $\Delta W =$

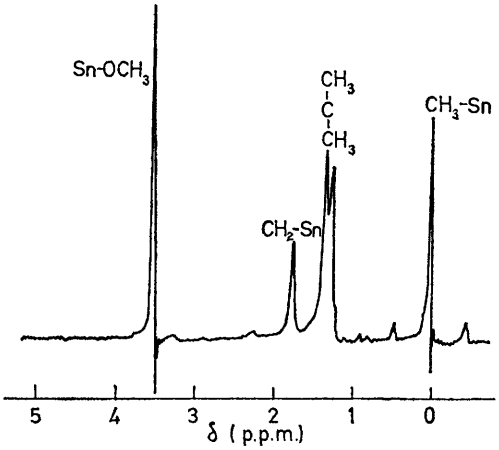


FIGURE 1 ^{1}H N.m.r. spectrum (high-field portion) of compound (4a) in 3M-benzene solution

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0·95 Hz, and from expression (2)[12] where τ is the mean

$$\tau = 1/\pi \,.\, \Delta W \qquad (2)$$

lifetime, an inversion rate $p(= 1/\tau)$ close to 3 s^{-1} is estimated, in agreement with the conclusions derived from peak separation. These approximate estimates show that the rates of intermolecular exchange and inversion of configuration differ considerably, and in alkoxystannanes each exchange is not necessarily accompanied by an inversion of configuration at the tin atom.

In compound (4b) the long-range coupling constant $J(^{117/119}Sn{-}O{-}C{-}H)$ (37 Hz) was observed in 2M solution, indicating that the intermolecular exchange rate should be lower than 80 s^{-1}. Probably in more dilute solutions the exchange rates are higher than this value, but unfortunately the complexity of satellites does not allow one to draw definite conclusions regarding this point. On the other hand, the inversion rate, estimated as for compound (4a), gives a value very close to that obtained for this compound. It seems therefore that the size of R is more important in determining the exchange than the inversion rate. Probably for R = Bu^t [compound (4c)] the exchange rate is even smaller, but this cannot be verified experimentally since no tin satellite is observed for this group. This seems reasonable, however, in view of results previously reported[7] which show that the exchange rate is strictly connected to the size of R. The inversion rate for compound (4c) is also very near to that estimated for compound (4a). Comparable inversion rates have also been estimated for derivative (4d), but it was not possible to determine the exchange rate. It may be supposed, however, on the basis of the results obtained[5] for organotin alkoxides where electronegative groups are present in R, that exchange should be slower than for compound (4b), since the phenyl and isopropyl groups should be of comparable size, but the electron-withdrawing character of the phenyl group should lower the exchange rate in compound (4d). For the exchange process a mechanism involving an intermediate of type (3) can be postulated; this assumption accounts for the decrease in the exchange rate when the size of R increases. The inversion should be ascribed to nondissociative positional exchange of the groups in this intermediate which should have a spatial arrangement very similar to intermediate (2) (double trigonal bipyramid). Apart from the OR groups, since in all derivatives of type (4) the same groups are involved in the postulated inversion mechanism, it is not surprising that these compounds show very similar inversion rates.

A different situation should be found when a certain amount of free ligand is added to the organotin alkoxides. Addition of the corresponding R–OH to compounds (4) should break the intermolecular bonds present in intermediate (3) and associate species containing ligand molecules should be formed. Solutions in benzene of different molar ratios of compound (4a) and methanol (2 : 1, 1 : 1, 1 : 2) have been studied and it was observed that changes occur when the mixture is diluted with the solvent. For all the molar ratios considered, the diastereotopic methyl groups give separate signals in dilute solution but coalescence is observed as concentration increases. In Figure 2

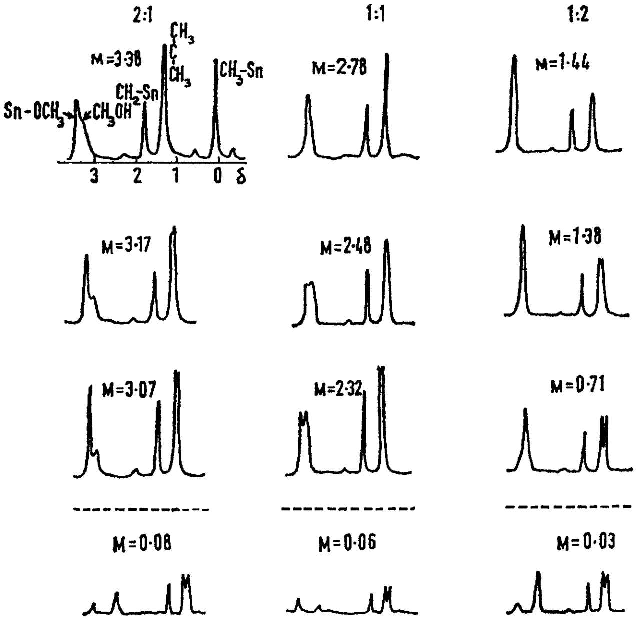

FIGURE 2 Changes of ^1H n.m.r. signals for mixtures of compound (4a) and methanol at different molar ratios as a function of concentration in benzene. M Refers to the molarity of compound (4a) relative to the solvent

TABLE 2

Exchange and inversion rates[a] measured at 28 °C for mixtures of compound (4a) and methanol in benzene solution at different concentrations [M refers to the molarity of (4a) in benzene solution]. C is the molar ratio (4a): methanol

Exchange			Inversion	
M	Rate (s^{-1})		M	Rate (s^{-1})
		$C = 2 : 1$		
3·38[b]	70		3·2[b]	10
3·18	8·5		1·27	3·1
3·07	5·9		0·63	2·1
1·27	3		0·315	1·9
0·63	2·8			
0·31	2·5			
		$C = 1 : 1$		
2·78[b]	80		2·48[b]	10
0·465	11		0·465	2·75
0·232	9·8		0·232	2·7
0·116	9·7			
		$C = 1 : 2$		
0·710[b]	76		1·38[b]	10
0·110	28·3		0·85	4·8
0·055	26		0·79	4·25
0·027	23·5		0·71	3·9
			0·55	3·16

[a] These exchange rates refer only to the exchange of the methoxy-group between (4a) and methanol, the exchange of the methoxy-group between organotin molecules, which also occurs, not being included. The inversion rates include a contribution from both exchange mechanisms. [b] At these concentrations coalescence of the signals under investigation occurs and the reported rates were estimated by means of equation (1); all other rates were estimated by means of equation (2).

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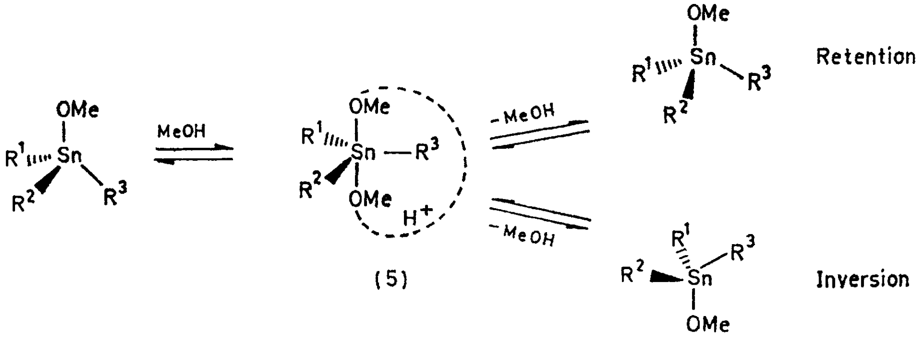
[12] J. W. Emsley, J. Feeney, and L. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, 1st edn., p. 481.

some representative portions of the spectra are collected which show the changes of the resonances of the groups in the different stannane–alcohol mixtures as function of their concentration in benzene. These results show that the inversion rate is much increased by the presence of alcohol. Since separate signals are also observed in dilute solution for the OMe group of methanol and that of stannane (4a) it is possible to estimate the rate of exchange between these molecules. Some values are recorded in Table 2 and were obtained by an approximate treatment as represented by equation (1). To interpret the increased inversion rate it is necessary to postulate a different path which involves intermediate (5) where a pentaco-ordinate tin atom is present; transetherification should occur when inversion takes place and the reaction should be catalysed by the acidic proton. For compounds (4b and c) no clear information about the exchange can be acquired owing to the complexity of the n.m.r. spectra obtained for the mixtures, while it is clearly observed that the diastereotopic methyl groups do not collapse under the conditions employed for compound (4a), not even when using the corresponding alcohol as a solvent. The formation of intermediate (5) is probably dependent on the steric hindrance of the group OR both on alcohol and stannane. It is interesting to note that it has been observed [8] in stannylamines that exchange and transamination reactions depend on the size of groups bonded to nitrogen, while the second process is always slower than the first. This should explain why in our compounds, according to the scheme suggested, inversion becomes rapid when transetherification becomes faster. Of course this mechanism of inversion of configuration should be different from that involving exchange through intermediate (3), an exchange which also takes place in the presence of alcohol, but does not contribute to the inversion process above the limit estimated when alcohol is not present.



Compound (4d) in the presence of phenol shows coalescence, as expected on the basis of the scheme suggested, since the catalytic action of the acidic proton should promote a rapid stannane–phenol exchange and make the transetherification faster.

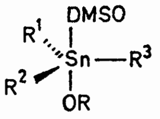
The effect of addition of methanol to compounds (4b—d) has also been investigated. Transetherification occurs for compounds (4b and c) and the ratios of the compounds formed, determined by n.m.r. analysis, are reported in Table 3. These figures refer to an equilibrium since the transetherification is reversible. As regards the behaviour of compound (4d), where methanol does not remove the OPh group, it should be noted that starting from the corresponding 1 : 1 Sn–OMe : PhOH mixture, the Sn–OPh derivative is formed quantitatively. While the different behaviours of compound (4b and c) with respect of methanol should be largely accounted for by the steric effects of the OR groups, the main reason for these equilibria should be different, particularly in view of the behaviour of compound (4d). Most probably, in all the compounds examined, intermediates of type (5) are formed by nucleophilic attack of OR^- ions, OPh^- in the case of phenol, and the transetherification equilibrium depends on the mass law; the phenoxide ions, which are present in higher amounts than the corresponding alkoxide ions, should be able to remove methanol, which is less dissociated.

TABLE 3

Equilibrium composition of the mixtures formed from compounds (4) and methanol

Starting mixture	Equilibrium composition
$\underset{/}{\overset{\backslash}{-}}$Sn–O–$Pr^i$–MeOH	$\underset{/}{\overset{\backslash}{-}}$Sn–O–$Pr^i$ + $\underset{/}{\overset{\backslash}{-}}$Sn–OMe ~50% ~50%
$\underset{/}{\overset{\backslash}{-}}$Sn–O–$Bu^t$–MeOH	$\underset{/}{\overset{\backslash}{-}}$Sn–O–$Bu^t$ + $\underset{/}{\overset{\backslash}{-}}$Sn–OMe ~15% ~85%
$\underset{/}{\overset{\backslash}{-}}$Sn–O–Ph–MeOH	$\underset{/}{\overset{\backslash}{-}}$Sn–O–Ph + $\underset{/}{\overset{\backslash}{-}}$Sn–OMe ~100%

Compounds (4) were also studied in the presence of a good ligand such as dimethyl sulphoxide (DMSO). In the corresponding trialkyltin halides [2-4] DMSO causes a marked increase of the inversion rate at the tin atom. For compounds (4a—c), addition of DMSO to the benzene solution, or even employing DMSO as solvent, does not cause coalescence of the diastereotopic methyl groups, while for compound (4d) coalescence is observed even in benzene solution with 1 : 1 Sn–OPh : DMSO. We believe that compounds (4a—c) have little tendency to co-ordinate DMSO and consequently no structure like (6) can be formed, in which stereochemical non-rigidity could lead to configurational inversion. This tendency should be higher when the OPh group is bonded to tin since this group should help to remove electron density from the tin atom through a conjugative process which gives a more Lewis-acid character to the tin atom. This last point will be cleared up through a study of complexation of simple organotin alkoxides and phenoxides with DMSO.



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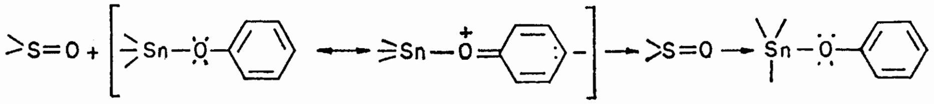

EXPERIMENTAL

The ^{1}H n.m.r. spectra were recorded on a JEOL JNM–C60–HL spectrometer. Standard solutions were prepared from anhydrous benzene and freshly prepared compounds in a dry-box; the solutions were diluted progressively by employing a graduated n.m.r. sample tube. Addition of alcohols or DMSO to the standard solutions was performed by employing calibrated microsyringes.

Compounds.—*2-Methyl-2-phenylpropyl chloride.* This was prepared according to Smith and Sellas.[13]

Methyldiphenyltin iodide. This was prepared in a similar manner to that reported for other tin compounds [14,15] starting from methyltriphenyltin and iodine in chloroform solution.

Methyl-(2-methyl-2-phenylpropyl)diphenyltin. Methyldiphenyltin iodide (51·7 g) in anhydrous tetrahydrofuran (150 ml) was added dropwise with stirring at room temperature to the Grignard reagent obtained in the usual way from 2-methyl-2-phenylpropyl chloride (41·9 g) in anhydrous tetrahydrofuran (280 ml). The mixture was refluxed for 3 h and then decomposed by adding dropwise a saturated aqueous NH_4Cl solution, cooling the reaction vessel externally. The organic layer was separated and the water solution extracted with ether. The organic portions were combined, dried ($MgSO_4$), and the solvent was evaporated. The volatile material was distilled at 50° and 1 mmHg, and the residue fractionated *in vacuo* to give the *product* (50·75 g, 95%), b.p. 150° at 0·015 mmHg, n_D^{22} 1·6008 (Found: C, 65·4; H, 5·55. $C_{23}H_{26}Sn$ requires C, 65·6; H, 6·2%).

Methyl-(2-methyl-2-phenylpropyl)phenyltin bromide. To the above compound (44·7 g) dissolved in methanol (200 ml) and chloroform (200 ml) and cooled at −60° was added dropwise (5 h) a bromine (17 g) solution in methanol (150 ml). Anhydrous solvents were employed. The mixture was allowed to reach room temperature slowly and then the solvent and low boiling compounds (bromobenzene) were evaporated. The residue was fractionated *in vacuo* to give the *product* (33·3 g, 75%), b.p. 125° at 0·01 mmHg, n_D^{21} 1·6000 (Found: C, 48·45; H, 4·2. $C_{17}H_{21}BrSn$ requires C, 48·1; H, 5·0%).

Methyl-(2-methyl-2-phenylpropyl)phenyltin methoxide (4a). Sodium methoxide, prepared from sodium (0·46 g) and anhydrous methanol (15 ml), was added over 2 h to a solution of the bromide (8·48 g) in anhydrous methanol (10 ml) with constant stirring under nitrogen. The mixture was refluxed for 1 h and the solvent was removed directly. Some anhydrous chloroform was added to the residue and solid sodium bromide was filtered with careful exclusion of moisture. The solvent was evaporated and the residue was fractionated twice *in vacuo* to give the *product* (3·6 g, 48%), b.p. 122° at 0·023 mmHg, n_D^{20} 1·5760 (Found: C, 58·05; H, 6·35. $C_{18}H_{24}OSn$ requires C, 57·65; H, 6·45%).

Compounds (4b and c) were obtained by a similar procedure employing the corresponding alkoxides. Compound (4b) (55%) had b.p. 102° at 0·007 mmHg, n_D^{20} 1·5570 (Found: C, 59·7; H, 7·3. $C_{20}H_{28}OSn$ requires C, 59·6; H, 7·0%). Compound (4c) (20%) had b.p. 114° at 0·008 mmHg, n_D^{20} 1·5880 (Found: C, 59·95; H, 7·2. $C_{21}H_{30}OSn$ requires C, 60·5; H, 7·25%).

Compound (4d) could not be obtained with satisfactory purity by the same process. Therefore, it was prepared in quantitative yield from equimolecular amounts of compound (4a) and phenol in anhydrous benzene by stirring the mixture for 2 h at room temperature. The solvent then evaporated and the compound was kept for 3 h *in vacuo*. Owing, probably, to the high b.p. the compound could not be purified by high vacuum distillation since decomposition occurs with redistribution of the groups around the tin atom. The compound did not show impurities in the n.m.r. spectrum.

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