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ORGANOMETALLIC COMPOUNDS
XXXII*. DIASTEREOTOPIC NONEQUIVALENCE IN ORGANOTIN CHEMISTRY

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SUMMARY

Diastereotopic nonequivalence is described for molecules of the type R'Me$_2$-SnCHY(CH$_3$) (with Y=C$_2$H$_5$, C$_6$H$_5$ and with various R' groups), for *meso*-R$''_2$ Sn(CHYCH$_3$)$_2$ (with R''=CH$_3$, CH$_2$C$_6$H$_5$) and for diastereoisomers such as Me$_{4-n}$-Sn(CHZCH$_3$)$_n$ [Z=Et, Pr; n=2,3] and Me-i-Pr-cyclo-HexSnCH(CH$_3$) (C$_6$H$_5$).

INTRODUCTION

Mislow has stated symmetry criteria to define equivalent, enantiotopic and diastereotopic groups[2]; Gutovsky has furthermore distinguished between the contribution to the nonequivalence due to the imbalance of the rotamer population and another contribution which he called "intrinsic"[3]. Numerous studies relate diastereotopic nonequivalences in organic chemistry[4], and at least two papers have shown experimentally the existence of intrinsic contributions[5].

On the other hand, only a few studies have appeared on diastereotopic nonequivalence in organometallic chemistry. Redl and Peddle claim to have measured the intrinsic nonequivalence of a silicon derivative[6], but their model is far from perfect[7]. Diastereotopic nonequivalences of protons or of methyl groups have been used[8] to show the optical instability of trialkyltin halides in the presence of traces of nucleophiles. Further work is being carried out in this field in our laboratory[9].

RESULTS AND DISCUSSION

Nonequivalence in sec-butyl- and (α-methylbenzyl)alkyldimethyltins

Table 1 lists the characteristics of the Sn–CH$_3$ signals in the NMR spectra of molecules of the following type:

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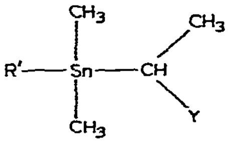
* For part XXXI, see ref. 1.



$Y = C_2H_5$ or C_6H_5
R' = alkyl, aryl

These molecules contain two methyl groups attached to the tin atom which cannot be superposed either by a C_n or by an S_n: these methyl groups are thus diastereotopic. The nonequivalence is experimentally detectable with a 60 MHz apparatus only when $Y = C_6H_5$ or, when $Y = C_2H_5$, if R' is sterically hindered. Furthermore, $\Delta\delta = 0$ for sec-butyldimethylphenyltin showing that an anisotropic group such as the phenyl group increases the nonequivalence when attached to the chiral center, and has a very small influence on it when attached to the pseudo-chiral center. Alkyldimethyl(α-methylbenzyl)tins with primary alkyl groups exhibit nonequivalences of about 2 Hz (6 Hz for secondary and 9 Hz for tertiary groups).

Table 1 shows that diastereotopic methyl groups exhibit different coupling

TABLE 1

DATA FOR THE METHYL GROUPS IN THE PMR SPECTRA OF $R'(CH_3)_2SnCH(CH_3)Y$ MOLECULES: DIASTEREOTOPIC NONEQUIVALENCE[a]

R'	$Y = C_2H_5$				$Y = C_6H_5$				
	$\delta(CH_3)$		$\Delta\delta_{AB}$	$J(^{119}Sn-CH_3)$	$\delta(CH_3)$		$\Delta\delta_{AB}$	$J(^{119}Sn-CH_3)$	
	A	B			A	B		A	B
Et	1.1		0	48.8	5.0	2.9	2.1	49.5	49.3
n-Pr	0.8		0	48.7	5.0	2.6	2.4	49.6	49.4
i-Pent					5.2	2.7	2.5	49.0	48.7
$Ph(CH_2)_2$	2.8		0	49.0	5.4	2.6	2.8	50.2	49.9
i-Bu	0.0		0	48.8	3.9	1.1	2.8	49.7	49.4
Neophyl	~3.9		~0.3	~49.5	22.1	17.0	3.1	50.5	50.0
i-Pr	~3.1		~0.2	~47.4	8.3	3.4	4.9	48.1	47.6
2-Bu					8.6 8.2	2.7 2.2	6.0 0.4	47.6	47.0
t-Bu	3.0	3.5	0.5	46	11.3	2.1	9.2	45.7	44.8
Ph	14.2		0	50.8	7.8	9.4	1.6	52.6	52.2
$(CO)_3CrPh$	27.8		0	55					
n-Bu	1.1		0	48.4					
2-Me-1-Bu	0		0	48.4					
Benz	4.1		0	49.0					
cyclo-Pent	2.9		0	48.4					
2-Pent(*threo*)	2.9			46.4					
2-Pent(*erythro*)	1.3	1.9	0.6	47.3					
3-Pent	2.9		0	46.9					
cyclo-Hex	~3.5		~0.2	47.1					
Naphthyl	22.1		0.7	47.4					
t-Pent	2.5	3.0	0.5	45.4					

[a] Solvent: CCl_4; all values in Hz.

constants. This is inconsistent with the existence of a simple linear relationship between $J(Sn{-}CH_3)$ and $\Sigma\sigma^*$ for the substituents on the tin atom[1], and also with Malinovski's additivity hypothesis[10].

Table 2 illustrates solvent effects on the nonequivalence: there is no apparent relationship between $\Delta\nu$ and the solvent properties.

TABLE 2

SOLVENT EFFECTS ON THE DIASTEREOTOPIC NONEQUIVALENCE FOR PHENYL- AND *tert*-BUTYLDIMETHYL-(α-METHYLBENZYL)TIN

Solvent	$\Delta\delta_{AB}$ (Hz)	
	R'=Ph	R'=t-Bu
Benzene	1.2	7.1
Toluene	1.3	7.7
Chlorobenzene	1.5	8.2
Methanol	1.7	10.0
tert-Butanol	1.7	9.4
Acetone	1.9	10.1
Carbondisulfide	1.8	9.4
Pyridine	1.5	8.3
Dimethyl sulfoxide	1.8	9.9
Chloroform	2.2	9.3
HMPT	1.8	9.8
Neat	1.4	8.7

TABLE 3

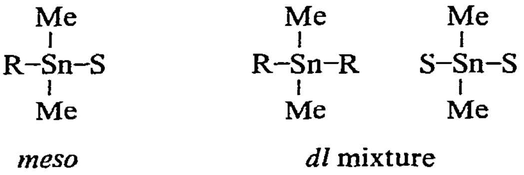
EFFECT OF TEMPERATURE ON THE DIASTEREOTOPIC NONEQUIVALENCE FOR ETHYL- AND *tert*-BUTYLDIMETHYL-(α-METHYLBENZYL)TIN

R'	Solvent	Diastereotopic nonequivalence (Hz) at temp. (°C) at					
		−90	−66	30°	+60	+100	+150
Et	CS_2	1.8	2.0	2.1			
	Neat			1.8	1.8	1.7	1.4
t-Bu	CS_2	7.6	8.9	9.3			
	Neat			8.8	8.5	7.9	7.3

Table 3 shows the effect of temperature on $\Delta\delta_{AB}$. A decrease of the temperature from 30° to −90°, seems to favor a rotamer characterized by a small intrinsic nonequivalence, since the nonequivalence decreases. At least one similar case has already been reported in the literature[11]. When the temperature is raised from 30° to 150°, the rotamer populations tend towards equality and $\Delta\delta_{AB}$ decreases.

The case of di-2-butyl-, di-2-pentyl- or bis(α-methylbenzyl)dimethyltins

These molecules contain two chiral centers (*R* or *S*)[12] attached to the tin atom; they can thus be found either as the *meso*-derivative or as a *dl* mixture:



$$\begin{array}{c}\mathrm{Me}\\|\\\mathrm{R{-}Sn{-}S}\\|\\\mathrm{Me}\end{array}\qquad\qquad\begin{array}{c}\mathrm{Me}\\|\\\mathrm{R{-}Sn{-}R}\\|\\\mathrm{Me}\end{array}\quad\begin{array}{c}\mathrm{Me}\\|\\\mathrm{S{-}Sn{-}S}\\|\\\mathrm{Me}\end{array}$$

meso *dl* mixture

In the *meso* compound, the two methyl groups cannot be superimposed by a C_n or an S_n and are thus diastereotopic. However, the two methyl groups in each of the two enantiomers of the *dl* mixture can be permutated using a C_2 axis, and are isochronous. A mixture of the two compounds gives three peaks in the methyl–tin region (see Table 4).

TABLE 4

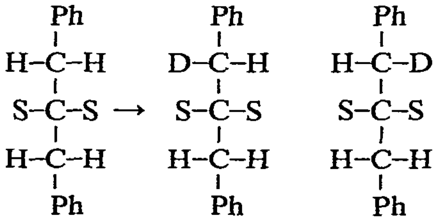
NMR SPECTRA OF $(CH_3)_2Sn[CH(CH_3)Y]_2$

Y	*dl*		*meso*			
	δ(Me) (ppm)	J(Sn–Me) (Hz)	δ[Me(1)] (ppm)	δ[Me(2)] (ppm)	J[Sn–Me(1)] (Hz)	J[Sn–Me(2)] (Hz)
Et	−0.038	44.8/46.8	−0.031	−0.046	44.8/46.8	44.4/46.4
n-Pr	−0.053		−0.048	−0.059	[a]	[a]
Ph	−0.16	46.0/48.1	−0.06	0.29	45.2/47.4	46.8/48.8

[a] Not resolved.

The case of dibenzylbis(α-methylbenzyl)tin

In *dl*-dibenzylbis(α-methylbenzyl)tin the two benzyl groups are equivalent, but the hydrogen atoms of a given benzyl group are diastereotopic, as can be shown formally by isotopic substitution[15]:



$$\begin{array}{c}\mathrm{Ph}\\|\\\mathrm{H{-}C{-}H}\\|\\\mathrm{S{-}C{-}S}\\|\\\mathrm{H{-}C{-}H}\\|\\\mathrm{Ph}\end{array}\longrightarrow\begin{array}{c}\mathrm{Ph}\\|\\\mathrm{D{-}C{-}H}\\|\\\mathrm{S{-}C{-}S}\\|\\\mathrm{H{-}C{-}H}\\|\\\mathrm{Ph}\end{array}\quad\begin{array}{c}\mathrm{Ph}\\|\\\mathrm{H{-}C{-}D}\\|\\\mathrm{S{-}C{-}S}\\|\\\mathrm{H{-}C{-}H}\\|\\\mathrm{Ph}\end{array}$$

A broad signal instead of the expected typical AB pattern is shown for these protons at 100 MHz.

In the *meso* derivative, the two benzyl groups are diastereotopic but the protons of the benzyl groups are enantiotopic. Experimentally, one finds two intense lines of the expected AB pattern.

The case of diastereoisomers

Generally, two diastereoisomers exhibit different physico-chemical properties: the benzyl groups of *dl*-dibenzylbis(α-methylbenzyl)tin react faster with bromine than those of the *meso* derivatives; these two compounds also have different NMR spectra (see Table 4). For methyltri-2-butyl or methyltri-2-pentyl, (2-butyl or 2-pentyl being either *R* or *S*), one has the systems as follows:

(1a) $MeSnR_3$ (2a) $MeSnR_2S$
(1b) $MeSnS_3$ (2b) $MeSnS_2R$

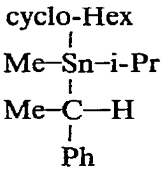
The methyl groups of (1a) and (1b) are enantiotopic, and thus isochronous in CCl_4. The methyl groups of (1) and (2) are diastereotopic by external comparison[2] and thus anisochronous (see Table 5).

TABLE 5

METHYL PART OF THE NMR SPECTRA OF $CH_3Sn[CH(CH_3)Y]_3$

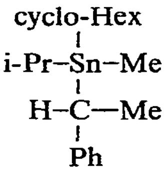
Y	$\delta(CH_3)(1)$ (ppm)	$J[SnCH_3(1)]$ (Hz)	$\delta(CH_3)(2)$ (ppm)	$J[SnCH_3(2)]$ (Hz)
Et	−0.056	42.2 44.0	−0.080	41.6 43.5
Pr	−0.083	41.3 43.2	−0.100	41.6 43.5

(α-Methylbenzyl)cyclohexylisopropylmethyltin also exists in the form of two diastereoisomeric (*erythro* or *threo*) *dl* mixtures:



$$\begin{array}{c}\text{cyclo-Hex}\\ |\\ \text{Me–Sn–i-Pr}\\ |\\ \text{Me–C–H}\\ |\\ \text{Ph}\end{array}$$

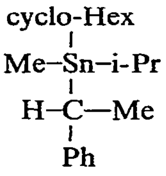
(3a)



$$\begin{array}{c}\text{cyclo-Hex}\\ |\\ \text{i-Pr–Sn–Me}\\ |\\ \text{H–C–Me}\\ |\\ \text{Ph}\end{array}$$

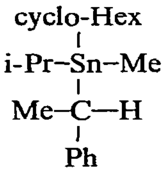
(3b)

erythro



$$\begin{array}{c}\text{cyclo-Hex}\\ |\\ \text{Me–Sn–i-Pr}\\ |\\ \text{H–C–Me}\\ |\\ \text{Ph}\end{array}$$

(4a)



$$\begin{array}{c}\text{cyclo-Hex}\\ |\\ \text{i-Pr–Sn–Me}\\ |\\ \text{Me–C–H}\\ |\\ \text{Ph}\end{array}$$

(4b)

threo

Thus there are two methyl–tin peaks, separated by 0.01 ppm and with coupling constants equal to 44.2 and 45.4 Hz respectively.

EXPERIMENTAL

Syntheses

The alkyl- and aryldimethyl(α-methylbenzyl)- and sec-butyltins have been synthesized by the following routes (refs. 13 and 1):

$$* \ AlkSnMe_3 \xrightarrow[MeOH]{Br_2} AlkSnMe_2Br \xrightarrow{PhYCH(CH_3)MgCl} AlkMe_2SnCHPhY(CH_3)$$

$$* \ (C_2H_5)(CH_3)HCSnMe_3 \xrightarrow[MeOH]{Br_2} (C_2H_5)(CH_3)HCSnMe_2Br \xrightarrow{AlkMgX}$$

$$\rightarrow AlkMe_2SnCH(C_2H_5)(CH_3)$$

$$* \ Ar_2SnMe_2 \xrightarrow[ROH]{Br_2} ArSnMe_2Br \xrightarrow{YCH(CH_3)MgCl} ArSnMe_2CHY(CH_3)$$

Furthermore,

$$PhMe_2SnCHY(CH_3) \xrightarrow{Cr_2(CO)_9} (CO)_3CrPhMe_2SnCHY(CH_3)$$

The structures of the new organotin molecules were confirmed by mass spectrometry[14] and their purities checked by GLC.

NMR spectra

NMR spectra were recorded on a Varian A60 with 5% solutions.

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