Investigations on Diastereoisomeric Tetraorganotin Compounds: the Use of ^{119}Sn NMR Spectroscopy for the Direct Determination of the Diastereoisomeric Composition

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The distinction of enantiomeric alkyl halides by conversion in non-associating diastereoisomeric tetraorganostannanes of the type $R_2SnR'_2$ (R = Ph, Bu and R' = 2-octyl, 2-butyl, but-3-en-2-yl, 2-methylbutyl) using ^{119} Sn NMR spectroscopy is described. An ^{119}Sn 'inverse gated decoupling' technique makes the direct quantitative analysis of the diastereoisomeric composition feasible. ^{13}C NMR data are reported and a diastereotopic non-equivalence of the R groups in the *meso*-derivatives of $R_2SnR'_2$ is described. Achiral diorganotin dichlorides were used as derivatizing agents.

The reaction of enantiomeric compounds with a chiral auxiliary and a subsequent NMR investigation is one of the most frequently applied techniques for the determination of the enantiomeric composition of chiral compounds.[1] Experiments in this way were carried out not only by ^{1}H and ^{13}C NMR spectroscopy, but also by ^{19}F, ^{31}P, ^{29}Si, ^{77}Se and ^{195}Pt NMR spectroscopy.[2,3] Although organotin compounds are very suitable derivatizing agents for organic compounds, little attention has been paid to the ^{119}Sn nucleus in this respect thus far.[4,5] The reason for this goes back to the association tendency of organotin compounds containing polar substituents that results in most cases in averaged signals in the NMR spectra. However, ^{119}Sn NMR spectroscopy has some favourable characteristics for the investigation of enantiomeric compounds: a large chemical shift range—*ca.* 2000 ppm—combined with a high sensitivity to small structural changes, a significantly higher relative NMR sensitivity of the ^{119}Sn isotope with respect to ^{13}C and the simplicity of the spectra. Pereyre *et al.* reported the high sensitivity of tin chemical shifts to small structural changes by distinguishing the three configurational isomers of tetra-*sec*-butyltin.[5] Using an 'inverse gated decoupling' pulse sequence no distortion of signal intensity by NOE is observed and direct quantitative analysis is feasible.

We report here the distinction of enantiomeric alkyl chlorides by conversion in non-associating diastereoisomeric tetraorganostannanes using achiral diorganotin dihalides as derivatizing agents, followed by ^{119}Sn NMR spectroscopic determination of the diastereotopic composition.

Experimental

All spectra were obtained with a Varian Unity 400 MHz spectrometer at 26 °C in $CDCl_3$ solution. The tetraorganostannanes were 0.2 mol dm^{-3} solutions in $CDCl_3$. Chemical shifts are reported with respect to internal Me_4Sn (^{119}Sn). In order to suppress the reduction in signal intensity due to the negative value of the nuclear Overhauser enhancement factor in ^{119}Sn NMR, an inverse gated decoupling technique was employed (acquisition time 0.425 s, pulse width 22 μs, relaxation delay 2 s).

Ph_2SnCl_2, Bu_2SnCl_2 and some alkyl chlorides were obtained commercially. 2-Octyl chloride, 2-methylbutyl chloride and (*S*)-(−)-2-methylbutyl chloride were obtained from the corresponding alcohols and thionyl chloride using standard methods. The tetraorganostannanes were prepared according to procedures given in the literature.[6,7]

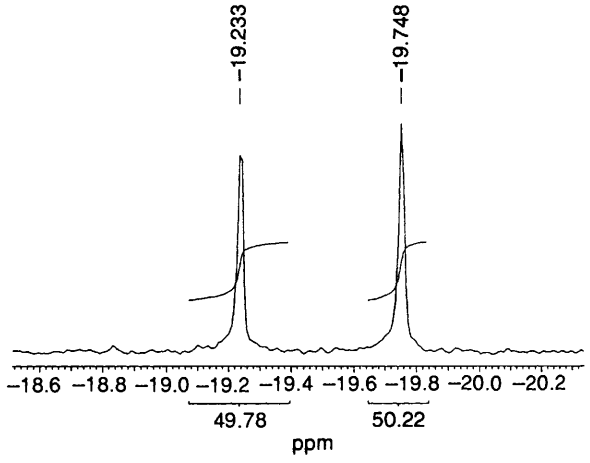

Fig. 1 149.16 MHz ^{119}Sn NMR spectra of **7** (number of scans = 100, total acquisition time = 4.7 min)

Results and Discussion

The Grignard reaction of optically active alkyl chlorides with diphenyltin dichloride or dibutyltin dichloride as a derivatizing agent (mole ratio 2:1) gives diastereoisomeric tetraorganostannanes [eqn. (1)] (compounds **1**–**8**). If the reaction is carried

$$2R'MgCl + R_2SnCl_2 \longrightarrow R_2SnR'_2 + 2\,MgCl_2 \quad (1)$$

R' = alkyl chain containing an asymmetric carbon;
R = Ph, Bu

out with an enantiomeric mixture of alkyl chlorides, the *meso*-form (*RS* and *SR*, respectively) and the racemic (±)-form (*SS* and *RR*, respectively) are produced due to the two chiral centres attached to the tin atom. Starting from a racemic mixture and assuming no enrichment of one of the enantiomers during the course of the reaction both diastereoisomeric compounds should be obtained in a 1:1 ratio.

The proof of the two diastereoisomeric forms succeeded both in the ^{1}H and ^{13}C NMR spectra and in the ^{119}Sn NMR spectra. Only selected signals of atoms near the asymmetric centre split up in the ^{1}H and ^{13}C spectra, whereas two separated signals are to be seen in the ^{119}Sn spectra of all investigated compounds (Figs. 1 and 2, Table 1). Signal separations are very small in the ^{1}H (0.8–16 Hz) and ^{13}C NMR spectra (3–20 Hz) due to tiny structural differences. A quantitative interpretation by integration in the ^{1}H spectra is impossible in most examples because of

Table 1 ^{119}Sn chemical shifts of tetraorganotin compounds, $R_2SnR'_2$

R	R'	Compound	$\delta(^{119}Sn)$
Ph	$-^1CH(^8CH_3)-^2CH_2-^3CH_2-^4CH_2-^5CH_2-^6CH_2-^7CH_3$	**1**	−80.4, −80.7
Ph	$-^1CH(^4CH_3)-^2CH_2-^3CH_3$	**2**	−81.6, −81.8
Ph	$-^1CH_2-^2CH(^5CH_3)-^3CH_2-^4CH_3$	**3**	−78.4, −78.6[b]
Ph	$-^1CH_2-^2CH(^5CH_3)-^3CH_2-^4CH_3$[a]	**4**	−78.7
Ph	$-^1CH(^4CH_3)-^2CH=^3CH_2$	**5**	−116.4, −116.7
Bu	$-^1CH(^8CH_3)-^2CH_2-^3CH_2-^4CH_2-^5CH_2-^6CH_2-^7CH_3$	**6**	−18.0, −18.4
Bu	$-^1CH(^4CH_3)-^2CH_2-^3CH_3$	**7**	−19.2, −19.7
Bu	$-^1CH(^4CH_3)-^2CH=^3CH_2$	**8**	−25.6, −25.9

[a] Enantiomerically pure (*S*)-(−)-2-methylbutyl chloride was used in reaction. [b] Assigned to the (±)-form.

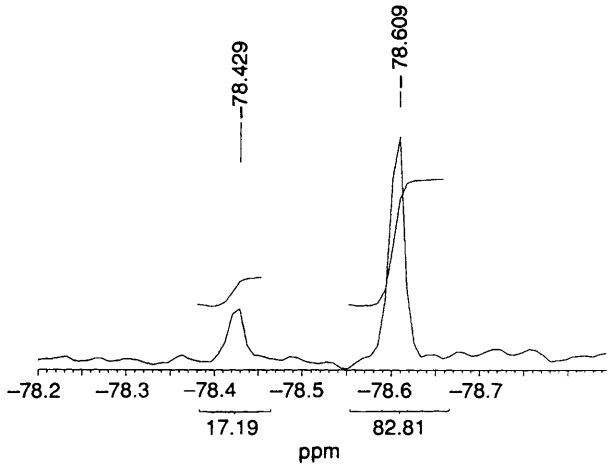

Fig. 2 149.16 MHz ^{119}Sn NMR spectra of **3** (0.5 mmol) and **4** (1 mmol) dissolved in 2 cm^3 $CDCl_3$ (number of scans = 100, total acquisition time = 4.7 min)

signal overlap. ^{1}H signals of the butyl groups and that of the chiral alkyl groups appeared in the same region in the case of dibutyldialkyltin compounds **6–8** and could therefore not even be assigned.

However, the quantitative determination of the diastereoisomeric ratio was unproblematic in the ^{119}Sn NMR spectra. The signal separations are in the range 30–80 Hz. Two distinct signals were observed (Figs. 1 and 2) and an integration is possible owing to the use of the 'inverse gated decoupling' technique. All recorded ^{119}Sn NMR spectra of $R_2SnR'_2$ derivatized from racemic mixtures of alkyl halides led to signal intensity ratios of 1:1. Using a mixture of **3** and **4**, signals belonging to the (±)-form could be assigned. No enrichment of one enantiomer took place during the course of the reaction.

The two R groups (Ph or Bu) of the *meso*-derivative are diastereotopic. They cannot be superimposed by a C_n or S_n symmetry operation. By contrast, these groups are isochronous in each of the enantiomers of the (±)-mixture. Using a C_2 axis they can be permuted.[8,9] Therefore three separate peaks—one for the (±)- and two for the *meso*-form—were observed in the ^{13}C chemical shift region of C_α or C_{ipso} of a mixture of the *meso*- and (±)-forms of compounds **2**, **3**, **6**. Otherwise the diastereotopic non-equivalence was not resolved in the ^{13}C and ^{1}H NMR spectra of the compounds investigated in this paper.

Conclusions

All the examples which have been discussed in this paper show that ^{119}Sn NMR spectroscopy is a useful tool for investigating diastereoisomeric tetraorganotin compounds. The high sensitivity of $\delta(^{119}Sn)$ to small structural changes may be convenient for quantitative analysis and differentiation of diastereoisomers. The use of achiral diorganotin dihalides as derivatizing agents presents an inexpensive method for the determination of the enantiomeric purity or diastereoisomeric composition of chiral alkyl halides, alcohols or related compounds.

Table 2 Values of the signal splitting $\Delta\delta$/Hz between the (±)- and *meso*-diastereoisomer for tetraorganotin compounds $R_2SnR'_2$ in ^{1}H, ^{13}C and ^{119}Sn NMR spectra

Compound	$\Delta\delta(^1H)$	$\Delta\delta(^{13}C)$	$\Delta\delta(^{119}Sn)$
1	1.6 (7-H), 1.6 (8-H)	4 (C_{ipso}), 6 (C-1), 6 (C-2)	48
2	0.8 (3-H)	6 (C_{ipso}), 9 (C-1), 4 (C-2)	33
3	12.0 (4-H), 16.0 (5-H)	5 (C_{ipso}), 6 (C-1), 12 (C-2), 3 (C-3), 6 (C-5)	27
5	2.0 (1-H), 2.4 (4-H)	8 (C-1), 3 (C-2), 11 (C-3), 20 (C-4)	52
6		3 (C-1), 5 (C-2)	52
7		6 (C-1), 4 (C-2), 3 (C-4)	78
8		6 (C-1), 3 (C-2), 18 (C-3), 17 (C-4)	48

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