# $^{119}$Sn NMR Spectroscopic Determination of Diastereomeric Ratio of Some Optically Active Organotin Compounds

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**Synopsis.** Diastereomeric ratio of optically active organotin compounds, $R^*_2SnX_2$ and $R^1R^2R^3SnR^*$, was successfully determined by means of $^{119}$Sn NMR spectra.

In the study of optically active organotin compounds, diastereomeric organotins play a versatile role[1)] in the asymmetric induction at tin, the optical resolution, and the determination of optical purity. Accordingly, it is of great importance to determine the diastereomeric ratio conveniently. $^1$H and $^{13}$C NMR spectra may be applicable in some cases where spectra are simple and signals due to diastereomers are fully separated though these requirements being not always fulfilled. Development of an alternative method, therefore, is highly desirable. Pereyre *et al.* have reported that diastereomers of $(s\text{-Bu})_4Sn$[2a)] and $R_3SnCH(CH_3)CH_2CO_2(-)Men$[2b)] (Men=menthyl) are distinguishable by means of $^{119}$Sn NMR spectra. In the course of our studies on optically active allyltin compounds,[3)] $R^*_2SnX_2$ and $R^1R^2R^3SnR^*$ proved to be versatile starting materials. Thus an effective method for quantitative determination of these diastereomers has been highly required for evaluating the degree of stereospecificity in the reaction of optically active allyltin compounds with aldehydes. Herein we wish to describe the usefulness of $^{119}$Sn NMR spectra for this purpose.

On account of facile optical resolution of 2-phenylbutyric acid with various degree of optical purity,[4)] 2-phenylbutyltin derivatives are suitable for attesting applicability of the $^{119}$Sn NMR spectroscopy to quantitative diastereomeric determination. As shown in Fig. 1, optically active $PB_2SnBr_2$ (**1a**) (PB=2-phenylbutyl) that was prepared employing optically pure (*R*)-2-phenylbutylmagnesium chloride exhibits a singlet at $\delta$ 58.3 while racemic **1a** gives rise to two signals at 53.3 and 58.3. Thus it is reasonably concluded that the signal at lower field can be attributed to the (*R,R*)- and (*S,S*)-isomers and the other at higher field to the (*R,S*)- and (*S,R*)-isomers. The results of other compounds are summarized in Table 1. Since each signal of $PB_2SnX_2$ is unambiguously assigned analogously, one can deduce the diastereomeric ratio from the relative integral ratio. The results obtained by employing a PB group with various degree of optical purity are depicted in Fig. 2. Apparently the observed values are in good agreement with calculated ones based on ee of the used PB group.

Of particular interest is that this method can be applied to estimation of the degree of asymmetric induction at tin in the following type of reaction that is the most common method for introduction of a chirality at tin.

$$\text{PhMeEtSnBr} + \text{RMgX} \longrightarrow \text{PhMeEtSnR}$$

**2a** R = PB
**b** = MB

Two optically active groups, (*R*)-PB and (*S*)-2-methylbutyl (MB) groups, were employed for this purpose. As shown in Table 1, $^{119}$Sn NMR spectra of these compounds indeed gave rise to two signals, indicating diastereomeric selectivity to be 54 and 53%, respectively. It is also to be noted that the diastereomeric ratio itself is not affected by optical purity of R.

## Experimental

$^{119}$Sn NMR spectra in proton gated decoupling mode were

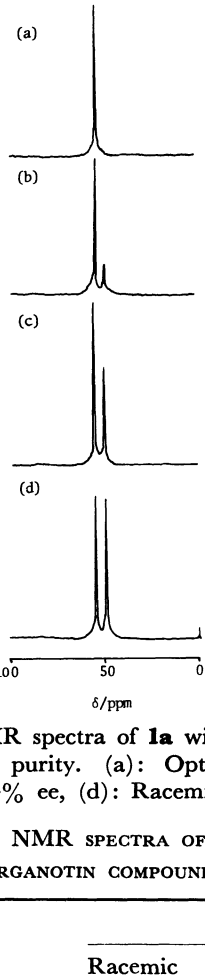


Fig. 1. $^{119}$Sn NMR spectra of **1a** with a PB group of different optical purity. (a): Optically pure, (b): 78% ee, (c): 24% ee, (d): Racemic.

TABLE 1. $^{119}$Sn NMR SPECTRA OF DIASTEREOMERIC ORGANOTIN COMPOUNDS

| Compound | | δ/ppm Racemic | δ/ppm Optically active |
|---|---|---|---|
| **1a** | $PB_2SnBr_2$ | 53.5, 58.3[a)] | 58.3 |
| **1b** | $PB_2SnCl_2$ | 90.5, 92.0[a)] | 92.0 |
| **1c** | $PB_2Sn(CH_2CH{=}CH_2)_2$ | −38.7, −39.1[a)] | −39.1 |
| **2a** | PhMeEtSnPB | −36.0, −36.9 (46 : 54)[b)] | −36.0, −36.9 (46 : 54)[b)] |
| **2b** | PhMeEtSnMB | −35.8, −36.0 (47 : 53)[b)] | −35.8, −36.0 (47 : 53)[b)] |

a) Relative integral ratio is *ca.* 1 : 1. b) Relative integral ratio.

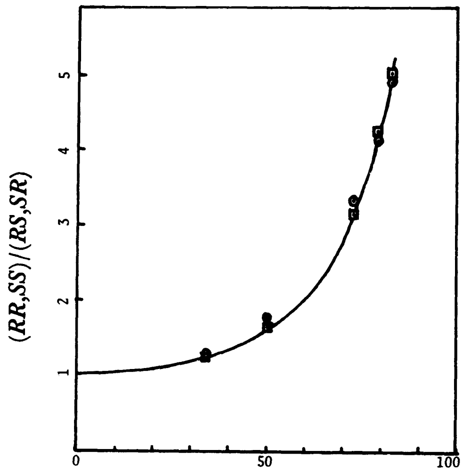


Fig. 2. Relation between ee of a PB group and (*RR,SS*)/(*RS,SR*) ratio. —— Calcualted; ⊙: Observed for **1a**, □: Observed for **1c**.

measured using a JEOL FX-100 spectrometer operating at 37.08 MHz at 22 °C. Field-frequency control was made with a deuterium-labelled solvent ($CDCl_3$) lock. The chemical shifts were determined relative to internal $Me_4Sn$, positive signs indicating low-field shifts from the reference, and were found to be accurate to ±0.1 ppm.

Optical resolution of 2-phenylbutyric acid was performed as the cinchonidine salt[4] into various degree of ee. Optically active 2-phenylbutyric acid thus obtained was converted into the corresponding chloride.[5] Optically active 2-methylbutyl bromide (ee>99%) was obtained by bromination of commercially available optically active 2-methyl-1-butanol (Aldrich Chemical Co.) with $PBr_3$.

*Preparation of 1a and 1b.* To a dichloromethane solution (10 $cm^3$) of **1c**[3] (467 mg, 1 mmol) was added dropwise bromine (320 mg, 2 mmol) at 0 °C. The reaction mixture was evaporated to leave an oil that was chromatographed on silica gel (500:1 hexane-ether) to give **1a** (491 mg, 90%); $^1$H NMR ($CCl_4$): $\delta$=0.70 (6H, t, $J$=7.0 Hz), 0.96—2.21 (8H, m), 2.21—2.88 (2H, m), and 6.58—7.22 (10H, m). Found: C, 44.42; H, 4.54%. Calcd for $C_{20}H_{26}Br_2Sn$; C, 44.08; H, 4.81%. $[\alpha]_D^{22}$ for optically active **1a** −38.9 (*c* 2.14, benzene).

The chloride **1b** was prepared analogously employing sulfuryl chloride in place of bromine in 65% yield; $^1$H NMR ($CCl_4$): $\delta$=0.70 (6H, t, $J$=7.2 Hz), 0.90—2.17 (8H, m), 2.17—2.97 (2H, m), and 6.62—7.24 (10H, m). Found: C, 52.88, H, 6.03%. Calcd for $C_{20}H_{26}Cl_2Sn$; C, 52.68; H, 5.75%. $[\alpha]_D^{22}$ for optically active **1b** −51.9° (*c* 1.02, benzene).

*Preparation of 2a and 2b.* To a THF solution (10 $cm^3$) of 2-phenylbutylmagnesium chloride prepared from 2-phenylbutyl chloride (471 mg, 2.79 mmol) and magnesium turnings (134 mg, 5.58 mmol), was added dropwise PhMeEtSnBr[6] (300 mg, 0.93 mmol) in THF (2 $cm^3$) at 0 °C. After being stirred for 2 h at room temperature, the reaction mixture was extracted with hexane-saturated ammonium chloride solution. The organic layer was washed with water and dried ($MgSO_4$). Evaporation and column chromatography (silica gel, hexane) of the resulting oil yielded **2a** (218 mg, 59%); $^1$H NMR ($CCl_4$): $\delta$=0.16, 0.18 (3H, s, diastereomeric), 0.66—2.10 (12H, m), 2.81 (1H, m), and 6.86—7.50 (10H, m). Found: C, 61.21; H, 7.60%. Calcd for $C_{19}H_{26}Sn$; C, 61.17; H, 7.22%.

The preparation of **2b** was carried out analogously employing 2-methylbutyl bromide in place of 2-phenylbutyl chloride in 63% yield; $^1$H NMR ($CCl_4$); $\delta$=0.48 (3H, s), 0.75—2.20 (16H, m), and 7.20—7.59 (5H, m). Found: C, 53.72; H, 8.30%. Calcd for $C_{14}H_{24}Sn$; C, 54.06; H, 7.78%.

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