Proof of Inversion of Configuration on Stannylation of a Configurationally Stable, Tertiary Benzyllithium Compound from a Single-Crystal X-Ray Structure Analysis**

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Abstract: Configurationally stable, dipole-stabilised benzyllithium compounds (*R*)- and (*S*)-**1b**, prepared by deprotonation of the corresponding esters with *s*BuLi in toluene/diethyl ether (5:1), reacted with (−)-menthyldimethyltin bromide to afford the stannanes (−)-**3** and (+)-**4**, respectively. A single-crystal X-ray structure analysis of compound (−)-**3** proved that stannylation occurred with inversion of the configuration at the benzylic centre, assuming retention for the deprotonation step. Lithio-destannylation and deuteration with MeOD follow a retentive course.

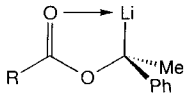
Keywords
benzoic acids · carbanions · lithiation · stannylation · stereochemistry

Introduction

A variety of carbanions with different metals as counterions react with trialkyltin halides to give stannanes (stannylation). These stannanes can be transmetallated with alkyl lithium compounds, preferably *n*BuLi, to regenerate the starting carbanion (lithio-destannylation). This sequence is of preparative value for the generation of certain salt-free organolithium compounds.[1] As long as only racemic carbanions were available, the question of stereochemistry of these reactions could not be addressed. Still's discovery of configurationally stable α-alkoxy anions[2] in 1980 was the starting point for the chemistry of other configurationally stable heteroatom-substituted carbanions having an oxygen,[3] a nitrogen,[4, 5] or a sulfur[6] substituent. The most prominent among these are the enantiomerically enriched α-lithiated *O*-alkylcarbamates[3] and *N,N*-dialkylcarbamates[4] prepared by enantioselective deprotonation with BuLi/(−)-sparteine. This base can deprotonate *N*-Boc-*N*-alkyl-[7] and *N*-Boc-*N*-(*p*-methoxyphenyl) benzylamine[8] so that they can react with electrophiles enantioselectively. The latter substrate was stannylated with inversion of configuration and transmetallated with retention, based on an X-ray structure analysis (anomalous dispersion) of the intermediate stannane.[9] The stereochemistry (retention or inversion) of reactions of heteroatom-substituted carbanions with electrophiles, their configurational stability and mechanism of racemisation[10] became focal points. Hoffmann et al. developed a protocol for the investigation of the microscopic and macroscopic configurational stability of a chiral organolithium compound.[11] It is classified as microscopically configurationally stable if its rate of racemisation is small relative to the rate of addition to an electrophile. Hoffmann et al. introduced *N,N*-dibenzyl-phenylalaninal as a standard electrophile. Macroscopic configurational stability implies that a chiral organometallic species retains its configuration for minutes.

Short-lived, chiral, benzyl anions have been generated by in-situ deprotonation/reprotonation of phenylalkanes[12] and as intermediates[13] in the Haller–Bauer cleavage. Chiral α-oxybenzyl anions have been inferred in the Brook[14] and the phosphate–phosphonate rearrangement[15] as well as in the reverse processes.

Until recently, it was assumed that stannylation and lithio-destannylation occur with retention of configuration. At that time Hoppe et al. were studying the tertiary carbamoyloxy-substituted organolithium compound **1a**[16] (Scheme 1). This compound is configurationally stable and the stereochemistry of its reactions depends on the electrophile used. Inversion of configuration is observed for alkyl halides[17], methyl chloroformate, carbon dioxide, carbon disulfide, acetyl nitrile, acyl chlorides and isopropyl isocyanate, while retention is observed for methanol and acetic acid,[18] dimethyl carbonate and pyrocarbonate, carboxylic acid esters and mixed anhydrides.[16] The configurations were determined by chemical correlation.



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Scheme 1. Lithium-complexed dipole-stabilised carbanions. **1a**: R = *i*Pr$_2$N; **1b**: R = 2,4,6-*i*Pr$_3$H$_2$C$_6$.

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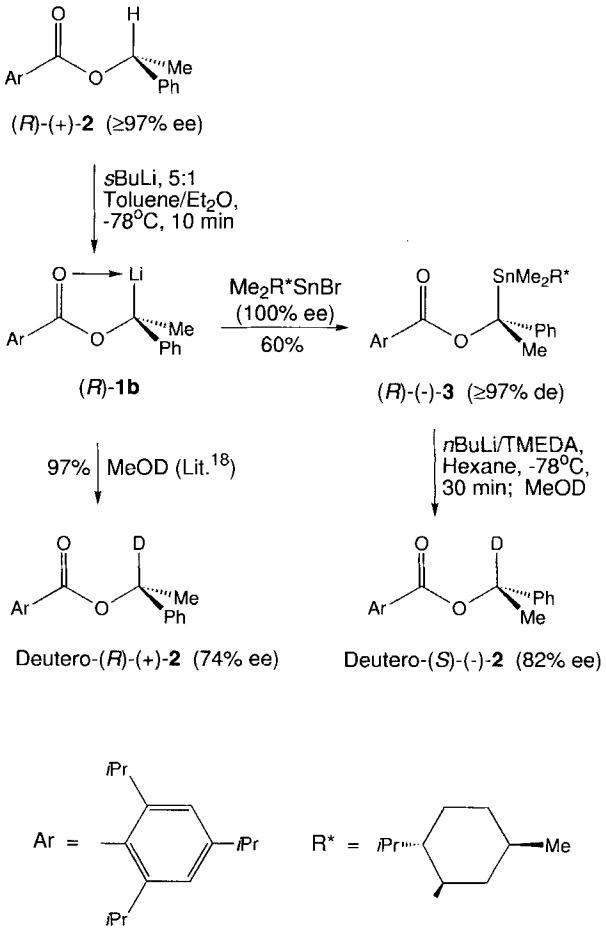
[**] Chiral Carbanions, Part 2. Presented at the Loschmidt Symposium, Vienna, June 1995; for Part 1, see ref. [18].

0947-6539/97/0310-1728 $ 17.50+.50/0

The reaction with triproduced a stannane with inversion of configuration, based on the assumption that deprotonation and lithio-destannylation follow a retentive course. The absolute configuration of the stannane was assigned by applying Brewster's rule, but was not rigorously secured (see ref. [22][16a]).

In Part 1 of this series,[18] we reported the configurational stability of the α-methylbenzyllithium **1b** with a 2,4,6-triisopropylbenzoyloxy substituent in toluene/diethyl ether (5:1) in the absence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and its reactions with MeOD, AcOD, dimethyl carbonate and methyl chloroformate, which occur with retention. Stannylation with trimethyltin chloride afforded a stannane, which, on transmetallation with BuLi and deuteration with AcOD, furnished an ester of opposite stereochemistry to the one used for the generation of **1b**. Up to now no case of protonation (deuteration) of an alkyllithium compound with inversion of configuration has been reported. Therefore, the net retention of all known deprotonation/reprotonation and deprotonation/deuteration sequences is commonly accepted as a proof of retention of configuration in the deprotonation reaction. Consequently, either stannylation or lithio-destannylation had to cause inversion. To solve this problem, we decided to use a homochiral trialkyltin halide for stannylation. This would facilitate the determination of the configurational stability of **1b** by use of a diasteomeric excess and of the absolute configuration by X-ray structure analysis—if at least one of the diastereomers is crystalline. The organolithium compounds **1a** and **1b** were also silylated with trimethylsilyl chloride, but the stereochemistry of the reaction products is still open.



Scheme 2. Deprotonation of 2,4,6-triisopropylbenzoate (*R*)-(+)-**2**, stannylation with (−)-menthyldimethyltin bromide and lithio-destannylation of stannane (−)-**3** followed by treatment with MeOD.

Results and Discussion

Triisopropylbenzoate[17] (*R*)-(+)-**2** (*ee* ≥ 97%) was deprotonated with *s*BuLi in hexane in the presence of TMEDA at −78 °C for 2 min and then reacted with (−)-menthyldimethyltin bromide[19] (Scheme 2). This reagent can be easily prepared from homochiral (−)-menthol. It might also prove useful for the preparation of diasteromeric, separable stannanes which give chiral, non-racemic organolithium compounds on transmetallation. Flash chromatography of the crude product furnished a viscous oil, which was homogenous by TLC and was a mixture of the two inseparable diastereomers (−)-**3** and (+)-**4** (structure given in Scheme 3) in a ratio of 93:7 (*de* = 86%) as indicated by ^{1}H NMR spectroscopy. The signals of the diastereotopic methyl groups bound to the tin centre can be used for an easy determination of the two isomers. The ^{1}H NMR spectra (400 MHz) show singlets at $\delta = -0.04$ and -0.01 for stannane (−)-**3** and at -0.08 and 0.07 for (+)-**4**. Each of the four signals is flanked by $^{117/119}$Sn isotope-induced satellite doublets (^2J = 42.8–45.3 Hz). If the reaction is carried out in a solvent mixture of toluene/diethyl ether (5:1) in the absence of TMEDA, the yield of the viscous oil is 60% with *de* ≥ 97% and $[\alpha]_D^{20} = -60.53$ (*c* = 7.94 in acetone) (Scheme 2).

The ^{1}H NMR spectrum shows the signals for the methyl groups bound to tin at $\delta = -0.04$ and -0.01. The intermediate organolithium compound (*R*)-**1b** is only configurationally stable in toluene/diethyl ether (5:1) at −78 °C, but not in hexane/TMEDA.[18] Therefore, the diastereomeric excess in hexane/TMEDA is diminished relative to that in toluene/diethyl ether. Stannane (−)-**3** could be crystallised from ethanol and its specific rotation did not increase on recrystallisation.

An X-ray structure analysis of a single crystal of (−)-**3** revealed the structure given in Figure 1.[20] The crystal structure data are given in Table 1.

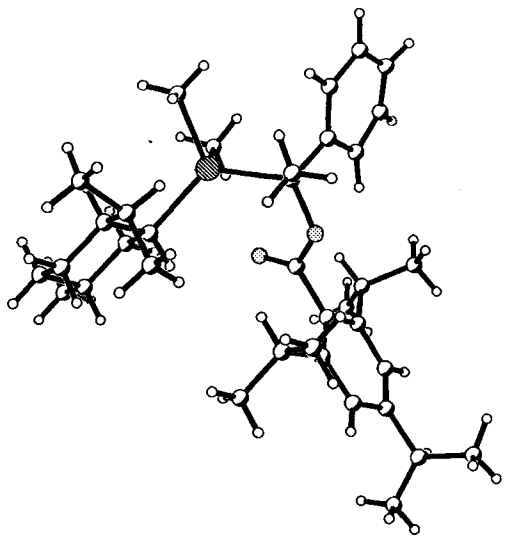


Figure 1. X-ray structure of stannane (−)-**3**.

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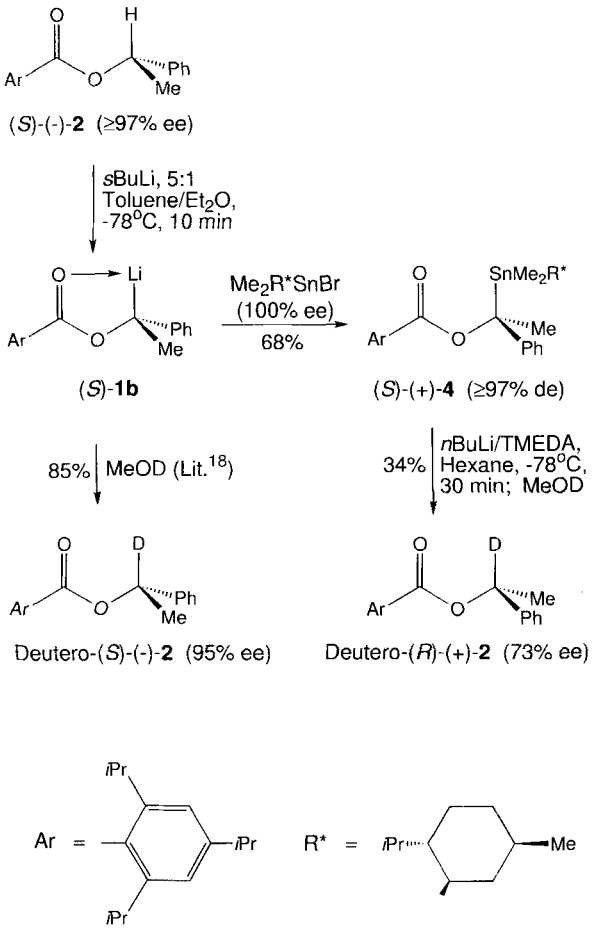
All substituents on the cyclohexane ring are equatorial, as expected, and the benzylic carbon has a (*R*)-configuration. Since the starting ester also had (*R*)-configuration, stannylation caused inversion of configuration (the descriptor does not change on going from the ester to the stannane (−)-**3** because the priorities are reversed).

Finally, stannane (−)-**3** was lithio-destannylated and treated with MeOD to give deutero-(*S*)-(−)-**2** (Scheme 2). Transmetallation was effected with a large excess of *n*BuLi/TMEDA in hexane at −78 °C and the reaction rate was slower than with the trimethyltin derivative.[18] Lithio-destannylation with *s*BuLi in toluene/diethyl ether (5:1) was not successful. The reaction was stopped by the addition of MeOD after 30 min before lithio-destannylation was complete. Unreacted starting material (37%) was recovered. The enantiomeric excess of deutero-(*S*)-(−)-**2** was 82%, determined by comparison with the specific optical rotation of the starting ester (*R*)-(+)-**2**. This protocol ensured only a small amount of racemisation of the intermediate benzyllithium compound. The deuterated ester, formed by deprotonation and treatment with MeOD, had the same configuration as the starting ester reported in Part 1.

Similarly, ester (*S*)-(−)-**2** was transformed into stannane (+)-**4**, a viscous oil, in 68% yield with $[\alpha]_D^{20} = +9.0$ ($c = 1.1$ in acetone) and $de \geq 97\%$ (Scheme 3).



Scheme 3. Deprotonation of 2,4,6-triisopropylbenzoate (*S*)-(−)-**2**, stannylation with (−)-menthyldimethyltin bromide and lithio-destannylation of stannane (+)-**4** followed by treatment with MeOD.

This stannane was lithio-destannylated and deuterated analogously to (−)-**3**. The ester deutero-(*R*)-(+)-**2** was obtained in 34% yield ($ee = 73\%$) and some stannane (40%) was recovered. Since these deuterations should occur with retention of configuration (see above), the Li–Sn exchanges in stannanes (−)-**3** and (+)-**4** must also proceed with retention of configuration.

Conclusions

Some possible reasons for the inversion of configuration of benzylic organolithium compounds are given. On the basis of calculations for the stabilisation of penta-coordinated carbonium ions that might serve as models for intermediates of the bimolecular aliphatic–electrophilic substitution (S_E2), Schleyer et al. found that retention and inversion of configuration are possible.[21] The metal ion and steric effects are major factors. Tertiary α-oxybenzyllithium compounds are configurationally less stable than secondary α-oxyalkyllithium compounds reacting with retention of configuration. No secondary, configurationally stable, benzylic carbanions with an α-oxygen are known which are macroscopically stable, only examples with α-nitrogen.[7, 8] The reduced configurational stability is also supported by X-ray structure analyses of benzylic lithium compounds. Resonance stabilisation in benzylic carbanions induces a flattening of the tetrahedral arrangement at the carbanionic centre and the activation barrier for an inversion of configuration is minimal.[22] Benzylic carbanions, generated as intermediates of the Haller–Bauer cleavage, are microscopically stable to some extent. The differing behaviour of α-oxyalkyl- and α-oxybenzyl carbanions as intermediates of the Brook and retro-Brook rearrangement is noteworthy.[23] Retention is observed for the former and inversion of configuration for the latter. Dialkylphosphoryloxy-substituted benzyllithium compounds rearrange with retention to isomeric phosphonates.[15] These examples demonstrate that the stereochemistry for the reaction of benzylic carbanions with electrophiles is sensitively influenced by various factors and has to be determined independently for each individual case.

Experimental Section

General: For thin layer chromatography (TLC), pre-coated plates (0.25 mm, silica gel 60, F_{254}, Merck) were used. Spots were visualised by UV and/or spraying with a 2% solution of $Ce^{IV}SO_4 \cdot 4H_2O$ in 2N H_2SO_4 and heating on a hot plate. Flash chromatography was performed on Merck silica gel 60 (0.040–0.063 mm) and mixtures of petroleum ether (boiling range 60–95 °C) and diethyl ether as eluents. Infrared spectra were recorded with a Perkin–Elmer FT 1600 IR Spectrometer. A solution of the sample in Uvasol chloroform was applied to a silicon plate[24] and the solvent was allowed to evaporate before the spectrum was recorded. ^1H and ^{13}C (*J*-modulated) NMR spectra were measured on a Bruker AC 250 F or AM 400 WB spectrometer. Chemical shifts (δ) are expressed downfield relative to TMS as an internal standard. Optical rotation was determined with a Perkin Elmer polarimeter 141 (1 dm cell). The melting point was measured with a Reichert Thermovar instrument and was uncorrected. Reactions were carried out in dry solvents under an atmosphere of argon. Hexane was dried over molecular sieves (4 Å). Diethyl ether was distilled from $LiAlH_4$ and toluene from sodium.

Preparation of stannanes (−)-3 and (+)-4: Organolithium compound (*R*)-**1b** was prepared by deprotonation (10 min) of ester (*R*)-(+)-**2** (1.058 g, 3 mmol, $ee \geq 97\%$) in a mixture of dry toluene (15 mL)/dry diethyl ether (3 mL) with

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*s*BuLi (12% solution in cyclohexane/hexane 92:8, 4.5 mL, 6 mmol) at −78 °C according to the procedure given in the literature.[18] (−)-Menthyldimethyltin bromide (2.58 g, 7 mmol) dissolved in dry diethyl ether (2 mL) was added dropwise. When the colour had disappeared (15 min), the cooling bath was removed and the mixture allowed to warm to room temperature. Volatile components were removed on a rotary evaporator. The residue was taken up in CH_2Cl_2. The solution was washed with 2N hydrochloric acid, a saturated aqueous solution of $NaHCO_3$, then water, dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/diethyl ether 20:1) to furnish stannane (−)-**3** (1.148 g, 60%) as a viscous oil.

In an analogous fashion, ester (*S*)-(−)-**2** (0.705 g, 2 mmol, *ee*≥97%) was transformed into stannane (+)-**4** (0.873 g, 68%), obtained as a viscous oil.

Stannane (−)-3: $R_f = 0.57$ (petroleum ether/diethyl ether 20:1); $[\alpha]_D^{20} = -60.53$ ($c = 7.94$ in acetone); crystallisation (twice) from ethanol gave a product with m.p. 74 °C; $[\alpha]_D^{20} = -60.50$ ($c = 2.82$ in acetone), *de*≥97% (^{1}H NMR); IR (Si): $\tilde{\nu} = 1698\ cm^{-1}$ (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.04$ (s, 3H, $Sn(CH_3)_2$; $^2J(^{117/119}Sn,H) = 43.3$ Hz, 45.3 Hz), −0.01 (s, 3H, $Sn(CH_3)_2$; $^2J(^{117/119}Sn,H) = 43.5$ Hz, 45.6 Hz), 0.77 (d, $^3J(H,H) = 5.9$ Hz, 6H, menthyl-$CH(CH_3)_2$), 0.85 (m, 2H, menthyl-H), 0.92 (d, $^3J(H,H) = 6.9$ Hz, 3H, menthyl-CH_3), 0.97 (dq, $^3J(H,H) = 2.5$ Hz, 12.8 Hz, 1H, menthyl-H), 1.23 (m, 3H, menthyl-H), 1.25, 1.28, and 1.33 (3×d, $^3J(H,H) = 6.9$ Hz, 18H, $CH(CH_3)_2$), 1.64 (m, 4H, menthyl-H), 1.87 (m, 1H, menthyl-H), 2.00 (s, 3H, $OCCH_3$; $^3J(^{117/119}Sn,H) = 45.8$ Hz), 2.90 (sept, $^3J(H,H) = 6.9$ Hz, 1H, $CH(CH_3)_2$), 3.07 (sept, $J = 6.9$ Hz, 2H, $CH(CH_3)_2$), 7.04 (s, 2H, H3 and H5 of ArCO), 7.04 (m, 2H, H_{arom}), 7.22 (m, 2H, H_{arom}), 7.29 (m, 1H, H_{arom}); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = -8.44$ ($Sn(CH_3)_2$; $^1J(^{117/119}Sn,C) = 274.2$ Hz, 288.4 Hz), −7.04 ($Sn(CH_3)_2$; $^1J(^{117/119}Sn,C) = 265.5$ Hz, 279.0 Hz), 15.80 (CH_3), 22.04 (CH_3), 22.47 (CH_3), 23.93 ($CH(CH_3)_2$), 23.95 ($CH(CH_3)_2$), 24.08 (2C, $CH(CH_3)_2$), 24.68 (2C, $CH(CH_3)_2$), 24.91 ($OCCH_3$; $^2J(^{117/119}Sn,C) = 13.7$ Hz), 26.56 (CH_2CSn; $^2J(^{117/119}Sn,C) = 74.0$ Hz), 31.33 (2C, Me_2CH), 33.42 (CH; $J(^{117/119}Sn,C) = 19.1$ Hz), 34.41 (Me_2CH–Ar), 35.08 (*C*HCSn; $^2J(^{117/119}Sn,C) = 70.2$ Hz), 35.27 (CH_2; $J(^{117/119}Sn,C) = 7.0$ Hz), 37.53 (SnCH; $^1J(^{117/119}Sn,C) = 422.2$ Hz, 444.0 Hz), 40.96 (CH_2; $J(^{117/119}Sn,C) = 22.9$ Hz), 45.85 (CH; $J(^{117/119}Sn,C) = 14.5$ Hz), 81.88 (OCMe), 120.99 (2C, HC_{arom}), 124.01 (2C, HC_{arom}), 125.21 (HC_{arom}), 127.84 (2C, HC_{arom}), 130.14 (C_{arom}), 145.06 (2C, C_{arom}), 146.66 (C_{arom}), 150.18 (C_{arom}), 171.98 (C=O; $^3J(^{117/119}Sn,C) = 16.0$ Hz); $C_{36}H_{56}O_2Sn$ (639.53): calcd C 67.70 H 8.83; found C 67.54, H 9.23. The crystal structure data for (−)-**3** are collected in Table 1.

Stannane (+)-4: $R_f = 0.57$ (petroleum ether/diethyl ether 20:1); $[\alpha]_D^{20} = +9.0$ ($c = 1.10$ in acetone), *de*≥97% (^{1}H NMR); IR (Si): $\tilde{\nu} = 1698\ cm^{-1}$ (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.08$ (s, 3H, $Sn(CH_3)_2$; $^2J(^{117/119}Sn,H) = 42.8$ Hz, 44.8 Hz), 0.07 (s, 3H, $Sn(CH_3)_2$; $^2J(^{117/119}Sn,H) = 43.8$ Hz, 45.8 Hz), 0.67 (d, $^3J(H,H) = 6.4$ Hz, 3H, menthyl-CH_3), 0.74 (d, $^3J(H,H) = 6.9$ Hz, 3H, menthyl-CH_3), 0.83 (d, $^3J(H,H) = 5.9$ Hz, 3H, menthyl-CH_3), 0.93 (m, 3H, menthyl-H), 1.16 (m, 4H, menthyl-H), 1.26, 1.28 and 1.34 (3×d, $^3J(H,H) = 6.9$ Hz, 18H, $CH(CH_3)_2$), 1.60 (m, 2H, menthyl-H), 1.71 (m, 1H, menthyl-H), 2.01 (s, 3H, $OCCH_3$; $^3J(^{117/119}Sn,H) = 43.3$ Hz), 2.90 (sept, $^3J(H,H) = 6.9$ Hz, 1H, $CH(CH_3)_2$), 3.08 (sept, $J = 6.9$ Hz, 2H, $CH(CH_3)_2$), 7.04 (s, 2H, H3 and H5 of ArCO), 7.12 (m, 2H, H_{arom}), 7.20 (m, 2H, H_{arom}), 7.29 (m, 1H, H_{arom}); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = -8.03$ ($Sn(CH_3)_2$; $^1J(^{117/119}Sn,C) = 286.8$ Hz, 300.6 Hz), −7.45 ($Sn(CH_3)_2$; $^1J(^{117/119}Sn,C) = 261.0$ Hz, 273.1 Hz), 15.94 (CH_3), 21.87 (CH_3), 22.60 (CH_3), 23.92 ($CH(CH_3)_2$), 23.94 ($CH(CH_3)_2$), 24.05 (2C, $CH(CH_3)_2$), 24.69 (2C, $CH(CH_3)_2$), 24.97 ($OCCH_3$; $^2J(^{117/119}Sn,C) = 10.7$ Hz), 26.69 (CH_2CSn; $^2J(^{117/119}Sn,C) = 74.0$ Hz), 31.38 (2C, Me_2CHAr), 33.06 (CH; $J(^{117/119}Sn,C) = 17.5$ Hz), 34.40 (Me_2CH–Ar), 35.16 (*C*HCSn; $^2J(^{117/119}Sn,C) = 71.7$ Hz), 35.32 (CH_2; $J(^{117/119}Sn,C) = 7.0$ Hz), 37.17 (SnCH; $^1J(^{117/119}Sn,C) = 405.0$ Hz, 428.0 Hz), 41.11 (CH_2; $J(^{117/119}Sn,C) = 22.1$ Hz), 45.48 (CH; $J(^{117/119}Sn,C) = 15.3$ Hz), 81.92 (MeCO), 120.99 (2C, HC_{arom}), 123.96 (2C, HC_{arom}; $J(^{117/119}Sn,C) = 14.5$ Hz), 125.19 (HC_{arom}; $J(^{117/119}Sn,C) = 9.9$ Hz), 127.80 (2C, HC_{arom}; $J(^{117/119}Sn,C) = 7.6$ Hz), 130.12 (C_{arom}), 145.01 (2C, C_{arom}), 146.43 (C_{arom}), 150.18 (C_{arom}), 172.04 (C=O; $^3J(^{117/119}Sn,C) = 16.8$ Hz).

Table 1. Crystal structure data for (−)-**3**.

formula	$C_{36}H_{56}O_2Sn$
M_r	639.53
T [°C]	20(2)
crystal size [mm]	0.60 × 0.52 × 0.45
crystal system	monoclinic
space group	$P2_1$
a [Å]	13.161(2)
b [Å]	8.874(1)
c [Å]	15.504(3)
β [°]	91.44(1)
V [Å^3]	1810.2(5)
Z	2
ϱ_{calcd} [g cm^{-3}]	1.173
radiation	$Mo_{K\alpha}$
λ [Å]	0.71069
scan mode	ω-scan
ω (max) [°]	24
reflections collected	3161
independent reflections	3040 [$R_{(int)} = 0.0146$]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3037/1/355
R	0.034
$wR2$	0.069
residual electron density [e Å^{-3}]	0.355/−0.289

Lithio-destannylation of (−)-3 and (+)-4 followed by addition of MeOD: A solution of *n*BuLi in hexane (1.6M, 3.75 mL, 6 mmol) was added dropwise to a solution of (−)-**3** (0.242 g, 0.38 mmol), and TMEDA (0.9 mL, 6 mmol) in dry hexane (5 mL) at −78 °C under argon. After 30 min MeOD (0.5 mL) was added. The reaction mixture was concentrated in vacuo and CH_2Cl_2 and 2N HCl were added to the residue. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were washed with a saturated solution of $NaHCO_3$, then dried ($MgSO_4$) and concentrated on a rotary evaporator. Flash chromatography of the residue (petroleum ether/diethyl ether 20:1) afforded the starting stannane (−)-**3** (0.09 g, 37%; $R_f = 0.67$) and deutero-(*S*)-(−)-**2** {0.14 g (26%); *ee* = 82%; $R_f = 0.38$; $[\alpha]_D^{20} = -15.9$ ($c = 1.72$ in acetone)}.

Similarly, stannane (+)-**4** (0.256 g, 0.40 mmol) was transformed to deutero-(*R*)-(+)-**2** {0.141 g (34%); *ee* = 73%; $[\alpha]_D^{20} = +14.4$ (c = 2.41 in acetone)}. Some stannane (+)-**4** (0.102 g, 40%) was recovered.

Acknowledgements: We thank the Fonds zur Förderung der wissenschaftlichen Forschung (Projects Nos. 6537C and P8671-MOB) and the Österreichischen Nationalbank (Project No. 5444) for support, and a referee for helpful comments.

Received: March 25, 1997 [F650]

[1] M. Pereyre, J.-P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworths, **1987**.
[2] W. C. Still, C. Sreekumar, *J. Am. Chem. Soc.* **1980**, *102*, 1201–1202.
[3] D. Hoppe, H. Ahrens, W. Guarnieri, H. Helmke, S. Kolczewski, *Pure Appl. Chem.* **1996**, *68*, 613–618.
[4] P. Beak, A. Basu, D. J. Gallagher, Y. S. Park, S. Thayumanavan, *Acc. Chem. Res.* **1996**, *29*, 552–560.
[5] a) R. E. Gawley, Q. Zhang, *J. Org. Chem.* **1995**, *60*, 5763–5769; b) R. E. Gawley, Q. Zhang, *Tetrahedron* **1994**, *50*, 6077–6088; c) V. K. Aggarwal, *Angew. Chem.* **1994**, *106*, 185–187; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 175; d) W. H. Pearson, A. C. Lindbeck, J. W. Kampf, *J. Am. Chem. Soc.* **1993**, *115*, 2622–2636.
[6] a) H.-J. Gais, G. Hellmann, *J. Am. Chem. Soc.* **1992**, *114*, 4439–4440; b) B. Kaiser, D. Hoppe, *Angew. Chem.* **1995**, *107*, 344–346; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 323.
[7] a) N. Voyer, J. Roby, *Tetrahedron Lett.* **1995**, *36*, 6627–6630; b) M. Schosser, D. Limat, *J. Am. Chem. Soc.* **1995**, *117*, 12342–12343.
[8] Y. S. Park, M. L. Boys, P. Beak, *J. Am. Chem. Soc.* **1996**, *118*, 3757–3758.
[9] Y. S. Park, P. Beak, *J. Org. Chem.* **1997**, *62*, 1574.
[10] a) T. Ruhland, R. Dress, R. W. Hoffmann, *Angew. Chem.* **1993**, *105*, 1487–1489; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1467; b) H. J. Reich, R. R. Dykstra, *ibid.* **1993**, *105*, 1489–1491 and **1993**, *32*, 1469.
[11] R. Hirsch, R. W. Hoffmann, *Chem. Ber.* **1992**, *125*, 975.
[12] D. J. Cram, C. A. Kingsbury, B. Rickborn, *J. Am. Chem. Soc.* **1961**, *83*, 3688–3696.
[13] J. P. Gilday, J. C. Gallucci, L. A. Paquette, *J. Org. Chem.* **1989**, *54*, 1399–1408.
[14] R. West, *Adv. Organomet. Chem.* **1977**, *16*, 1.
[15] F. Hammerschmidt, S. Schmidt, *Chem. Ber.* **1996**, *198*, 1503–1508.

  0947-6539/97/0310-1731 $ 17.50+.50/0

[16] a) D. Hoppe, A. Carstens, T. Krämer, *Angew. Chem.* **1990**, *102*, 1455–1456; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1424; b) A. Carstens, D. Hoppe, *Tetrahedron* **1994**, *50*, 6097 6108.
[17] C. Derwing, D. Hoppe, *Synthesis* **1996**, 149–154.
[18] F. Hammerschmidt, A. Hanninger, *Chem. Ber.* **1995**, *128*, 1069–1077.
[19] H. Schumann, B. C. Wassermann, *J. Organomet. Chem.* **1989**, *365*, C1–C5.
[20] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Crystallographic Data Centre as supplementary publication no. CCDC-100277. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).
[21] E. D. Jemmis, J. Chandrasekhar, P. v. Ragué Schleyer, *J. Am. Chem. Soc.* **1979**, *101*, 527–533.
[22] a) W. Zarges, M. Marsch, K. Harms, W. Koch, G. Frenking, G. Boche, *Chem. Ber.* **1991**, *124*, 543–549; b) W. Zarges, M. Marsch, K. Harms, G. Boche, *ibid.* **1989**, *122*, 2303–2309; c) W. Zarges, M. Marsch, K. Harms, F. Haller, G. Frenking, G. Boche, *ibid.* **1991**, *124*, 861–866; d) G. Boche, M. Marsch, J. Harbach, K. Harms, B. Ledig, F. Schubert, J. C. W. Lohrenz, H. Ahlbrecht, *ibid.* **1993**, *126*, 1887–1894.
[23] R. Hoffmann, R. Brückner, *Chem. Ber.* **1992**, *125*, 2731–2739.
[24] W. Mikenda, *Vib. Spectrosc.* **1992**, *3*, 327–330.

  0947-6539/97/0310-1732 $ 17.50+.50/0