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Enantiomerically Enriched 1-(*N,N*-Diisopropylcarbamoyloxy)-1,3-dimethylallyllithium: Stereochemistry of the Stannylation, Titanation, and the Homoaldol Reaction

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Summary. Contrarely to our former assumption[1,3], the title compounds **3** and **9** [(2*E*)- and (2*Z*)-isomer, (-)-sparteine or TMEDA complex] are substituted by means of trialkyltin halides in an *anti*-S_E' process. The optically active allylstannanes, thus produced, and aldehydes undergo a stereospecific homoaldol reaction under the influence of $TiCl_4$ which involves a second *anti*-S_E' transmetallation.

We recently reported the generation of chiral allyllithium derivatives which exhibit a remarkable degree of configurational stability by stereospecific deprotonation of optically active secondary *O*-2-alkenyl *N,N*-diisopropyl carbamates[1,2]. A more convenient approach consists in the kinetic resolution of the racemic carbamate *rac*-**1** by means of *n*-butyllithium/(-)-sparteine[3,4,5]. The chiral base system is capable of an efficient enantiomer recognition, deprotonating preferentially the precursor (*S*)-**1** to form the lithium complex (*S*)-**3**/(-)-**2** besides recovered (*R*)-**1** (Scheme 1).

Stannylation and Absolute Configuration of the Allylstannanes. The reaction with tributyltin- or trimethyltin chloride yields the optical active allylstannanes[3,6] (-)-**4a,b** and (+)-**5a,b**[3] (Table 1). The enantiomeric excesses of **4a** (≥ 80% *ee*) and **4b** (≥ 60% *ee*) could not be determined directly by the usual methods and are the minimal values, estimated from the enantiomerical purity of the homoaldol products, prepared therefrom (see below). The mixture of (*E/Z*)-isomers (-)-**4** and (+)-**5** bearing a stereogenic center of opposite absolute configuration at C-3 origins from the attack of the electrophile on both torsional isomers **A** and **B**. In the preliminary communications[2,3] we had assigned the (3*S*)-configuration to (-)-**4** (according to *ent*-**4** in Scheme 1), based on an extension of Brewster's rules[7] and on the stereochemical outcome of the $TiCl_4$-catalyzed homoaldol reaction, giving evidence for an overall stereoretention in the two transmetallation steps.

This led us to the assumption, that (-)-**4** and (+)-**5** arise from a *syn*-S_E' attack of the chlorostannane onto the alkyllithium (*S*)-**3**. During the further course of our work, doubts about the correct interpretation of the experimental results arose for the following reasons:

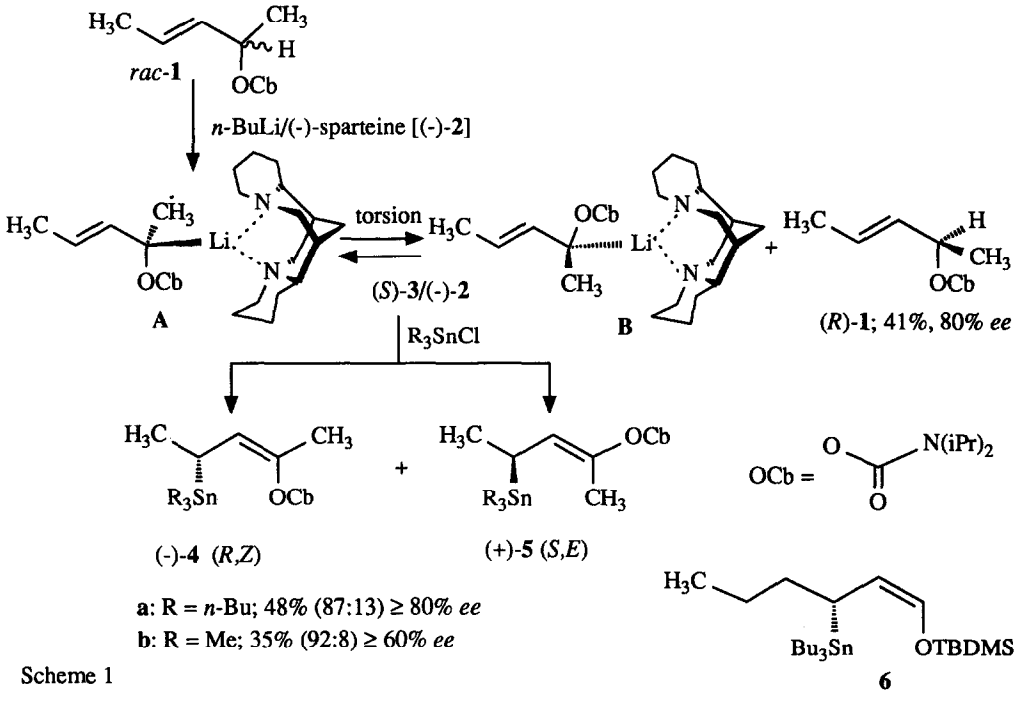
1. In the reaction of the lithium sparteine complex derived from the appropriate 2-butenyl *N,N*-diisopropyl carbamate[4a,b,c] with electrophiles, never suprafacial attack had been observed, presumably since the Lewis

acidity of the lithium cation is extinguished by the large complexing ligand.

2. Marshall and coworkers[8] reported some 1,3-trans-stannylations of (1-oxyallyl)stannanes proceeding in a strict *anti*-S_E' substitution.

3. The minus-rotatory γ-oxy-substituted allylstannane **6** was found to have (*S*)-configuration in a reliable stereochemical correlation carried out by the same author[6d].

Therefore, we undertook a reinvestigation on the stannane (-)-**4b**. Attempts to effect an uncatalyzed addition of (-)-**4** with benzaldehyde, which is expected to take place in a *syn*-S_E' process[6a-c], or to accomplish a trifluoroacetolysis (*anti* process[9]) were not successful.

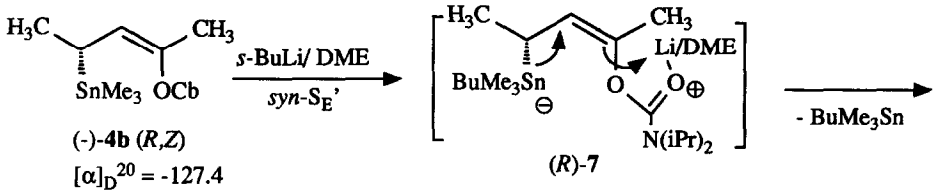


Scheme 1

In a further experiment (Scheme 2), (-)-**4b**, was treated with *sec*-butyllithium in 1,2-dimethoxyethane (DME)[10]. Restannylation of the intermediate ion pair **3**/DME gives the enantiomer (+)-**4b** with an overall chirality transfer of 61%. Thus, delithio-stannylation and destanno-lithiation take an opposite stereochemical course, one proceeds as an *anti*- and the other as *syn*-S_E' substitution. To which step is the *syn*-S_E' process related? All evidence points to the destanno-lithiation, as it was observed in a similar reaction sequence, performed with enantiomerically enriched lithio-benzyl carbamates[11]. To our best knowledge, no example for a tin-lithium exchange in 1-(oxy)-alkylstannanes to proceed with stereoinversion has been reported[12,4d,6a-c]. Unfortunately, no information is available in this respect for allylic substrates due to the configurational instability of the corresponding lithium derivatives. The tin-lithium exchange[12b] is assumed to occur through a lithium pentaalkylstannate of type (*R*)-**7**, which collapses with replacement of tetraalkylstannane by the lithium cation, "anchored" to the carbamoyl group, from the same face. This interpretation is a speculation, based on electrostatic arguments.

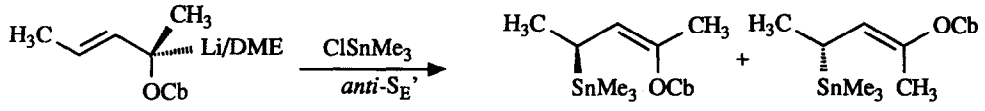
However, since the stereochemical relationship of the lithium compounds **3** (and as well, of the appropriate benzylic analogues[11]) with several substitution products has been established, the assumption of

the involvement of any *anti*-S_E' process in the destanno-lithiation leads to severe inconsistencies.



(-)-**4b** (*R*,*Z*)
$[\alpha]_D^{20}$ = -127.4

(*R*)-**7**



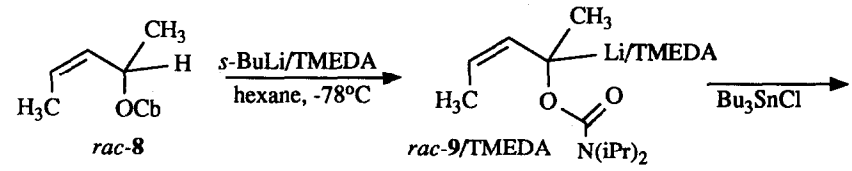
(*R*)-**3**/DME

(+)-**4b** (*S*,*Z*)
$[\alpha]_D^{20}$ = +67.0

(-)-**5b** (*R*,*E*)

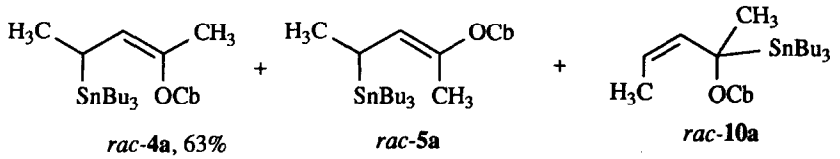
Scheme 2

Deprotonation and Stannylation of Enantiomerically Enriched (Z)-1-Methyl-2-butenyl Carbamates. The deprotonation of the racemic (*Z*)-carbamate *rac*-(*Z*)-**8** proceeds smoothly under the usual conditions (*s*-BuLi, TMEDA, hexane, at -78°C) to form on stannylation the γ-product *rac*-**4a** (Scheme 3 and Table 1) which is accompanied by small amounts of the (*E*)-isomer *rac*-**5a** and the α-substitution product (*Z*)-**10** (ratio 90:6:4, determined by GC). The by-products **5a** and **10** are difficult to separate in pure form. (*Z*)-**10** is recognized by the coupling constant $J_{2,3}$= 11.7 Hz in the ^{1}H-NMR spectrum. A distinction between the stannanes (*Z*)-**4a** and (*E*)-**5a** can be made on the basis of the ^{1}H,^{13}C-coupling constant $J_{H\text{-}2,C\text{-}1'}$ of 3.3 Hz in **4a** and 6.0 Hz in **5a** (*cis*- or *trans*-arrangement of H-2 and 1-CH_3, respectively).



rac-**8**

rac-**9**/TMEDA



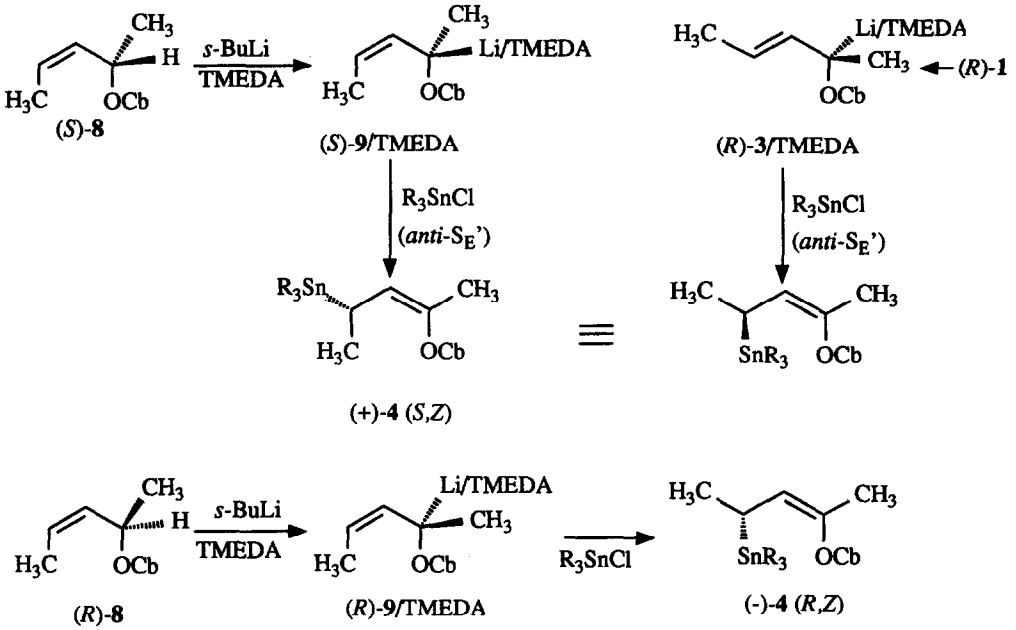
rac-**4a**, 63%

rac-**5a**

rac-**10a**

Scheme 3

The enantiomerically pure (*Z*)-carbamates (*S*)-**8** and (*R*)-**8**, easily available from alkyl lactates[13], were also subjected to a deprotonation/stannylation study. Scheme 4 and Table 1 collect the results (the by-products **5a** and **10** are omitted for the sake of clarity). (*S*)-**8** gives rise to (*S*,*Z*)-(+)-**4**, which also is formed from (*R*)-**1** via the carbanion (*R*)-**3**/TMEDA.



Scheme 4

yields see Table 1

Table 1. Allylstannanes **4** Prepared

educt	major product	R	yield (%)	ratio **4/5** [a]	**4**: $[\alpha]_D^{20}$ [b,d]	**4**: configuration	*ee* (%)
rac-**1**/(-)-**2**	(-)-**4a**	*n*-Bu	48[c]	87 : 13	-75 (CH_2Cl_2)	*R,Z*	> 80
(*R*)-**8** (100% *ee*)	(-)-**4a**	*n*-Bu	55	95 : 5	-101 (CH_2Cl_2)	*R,Z*	> 95[e]
(*S*)-**8** (100% *ee*)	(+)-**4a**	*n*-Bu	53	95 : 5	+101 (CH_2Cl_2)	*S,Z*	> 95[e]
rac-**8**	*rac*-**4a**	*n*-Bu	63	95 : 5	—	—	—
rac-**1**/(-)-**2**	(-)-**4b**	Me	35[c]	92 : 8	- 93 ($CHCl_3$)	*R,Z*	> 60
(*R*)-**8** (100%*ee*)	(-)-**4b**	Me	65	90 :10	- 127($CHCl_3$) [f]	*R,Z*	> 90[e]
(*R*)-**1** (90%*ee*)	(+)-**4b**	Me	52	g)	+ 133($CHCl_3$)	*S,Z*	≤ 90
(*S*)-**8** (100%*ee*)	(+)-**4b**	Me	61	90 :10	+ 138($CHCl_3$)	*S,Z*	≥ 90[e]

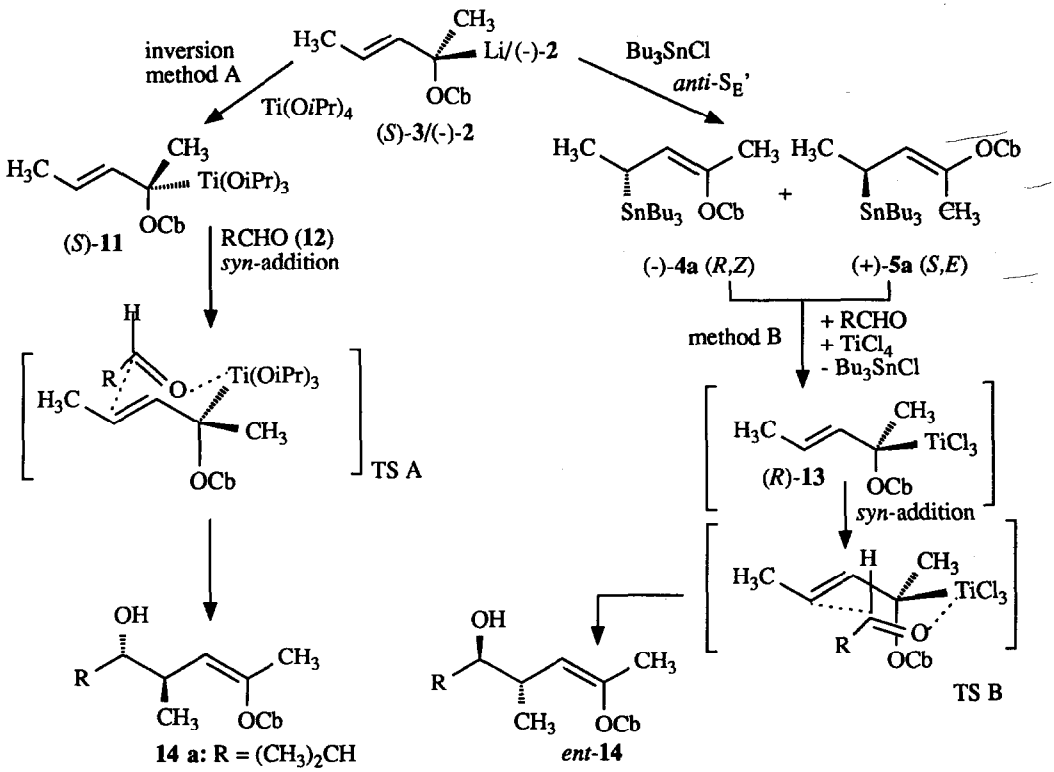
a) Determined by GC. b) Pure **4** (unless otherwise stated). c) Yields based on *rac*-**1**, which was used in excess. d) c= 1-3. e) Estimated by comparision of the optical rotation. f) The sample was contaminated by 3 % of (+)-**5b**. g) Not recorded.

From these experiments, the following becomes evident: The deprotonation of **8** proceeds with stereoretention as it was observed for (*R*)-**1**[1]. The four possible stereoisomers of the lithium complexes **9** and **3** [(*S,Z*), (*R,Z*), (*S,E*), and (*R,E*)] do not interconvert to a significant degree below -70°C in hexane solution. These processes would require the torsion of the 2,3-double bond[14] and the inversion of the

stereogenic center; both isomerizations are hampered by the close fixation of the lithium cation to the 1-position in the chelated ion pair[15]. Decreased configurational stability in solution is encountered in the lithium carbanions derived from primary 2-alkenyl[4a,b,14,15] and from some secondary 2-alkynyl carbamates, where the intermolecular cation exchange processes might be facilitated. Again, the stannylation of **9**/TMEDA takes place as *anti*-S_E' substitution.

Stereochemistry of the Lithium-Titanium and Tin-Titanium Exchange; Enantiodivergent Homoaldol Reaction. The homoaldol reaction[5] of titanated[16] (2*E*)-alkenyl carbamates with achiral aldehydes furnishes the (*Z*)-*anti*-diastereomers[18] with essentially complete simple diastereoselectivity. Similarly to allylboranes and -boronates[17], the carbonyl addition of allyltitanates[20] proceeds through a well-ordered six-membered pericyclic transition state[21]. As a result, an efficient self-immolative chiral induction ("chirality transfer") takes place, in which the absolute configuration of the metal-bearing stereogenic centre determines the face of the allylic double bond to be attacked in the *syn*-addition process[1a] (see transition states **A** and **B** in Scheme 5).

The lithium-titanium exchange of **3**/TMEDA by tetra(isopropoxy)titanium[16] (TIPT) is accompanied by stereoretention[1,3], whereas the appropriate 2-butenyllithium/ (-)-sparteine complex showed stereoinversion under the same conditions[4a-c]. When the complex (*S*)-**3**/(-)-sparteine is treated with TIPT, and then 2-methylpropanal is added, the minus-rotatory adduct **14a** is isolated with 36% yield (based on *rac*-**1**) and 75% *ee* (Scheme 5). Its absolute configuration (3*R*,4*S*)[1b] is correlated with titanium intermediate (*S*)-**11** through ts **A**, formed from lithium compound (*S*)-**3** with inversion.

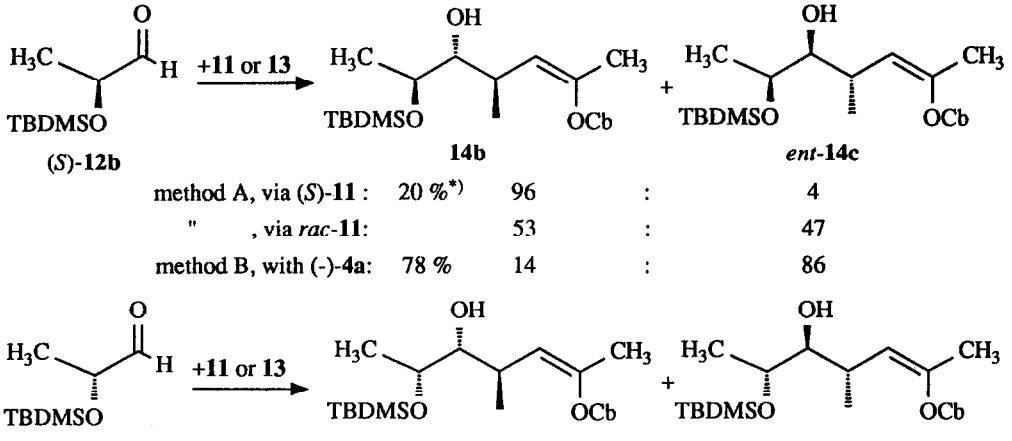


Scheme 5 36 %(based on *rac*-**1**), 75% *ee* **14a:** 74 % (based on **4**/**5**), 80% *ee*

The allylstannanes (-)-**4a** or (+)-**5a** do not undergo a thermal carbonyl addition[6] with benzaldehyde even at 150°C. It is known, that several Lewis acids catalyze this reaction even at low temperatures[22]. Most of the usual catalysts failed, however, when the stannane (*R,Z*)-(-)-**4a** (pure or contaminated with (*S,E*)-(+)-**5a** as obtained by the stannylation of (*S*)-**3**/(-)-sparteine) is treated with titanium tetrachloride in the presence of aldehyde **12a**, the enantiomeric homoaldol product *ent*-**14a** is isolated with 74% yield (based on **4/5**), and 80% *ee*[2]. The presence of only small amounts of *syn*-products (5%) excludes an open-chain pathway in the carbonyl addition. The stereochemical outcome requires the trichlorotitanium intermediate (*R*)-**13** which is one partner in ts **B**. Obviously, stereoisomers (-)-**4** and (+)-**5**, which differ in both absolute and double bond configuration, deliver in an *anti*-S_E'-process the same stereoisomer **13**, "neutralizing" the stereodivergency of the delithio-stannylation.

A further proof for the configuration of the involved titanium intermediates **11** and **13** was delivered by the utilization of both enantiomeric protected lactaldehydes[23] (*S*)- and (*R*)-**12b** for reaction partners in the homoaldol reaction[1b]. Due to the high degree of reagent-controlled stereoselectivity in the addition step, the problems of determining absolute configurations and enantiomer compositions are reduced to the analysis of relative configurations and diastereomer ratios in **14b**/*ent*-**14c** or **14c**/*ent*-**14b**, respectively. The preconditions - a minor influence of mutual kinetic resolution[24], a facile separation and safe structural assignment[25,26] for the diastereomers - were found to be given on several occasions.

Whereas the in-situ generated *racemic* reagents *rac*-**11** or *rac*-**13** with (*S*)-**12b** led to a essentially equal amount of the diastereomers **14b** and *ent*-**14c** (Scheme 6), method A yields **14b** and method B yields *ent*-**14c** in large excess. The analogous experiments with (*R*)-**12b** produce the enantiomers **14c** and *ent*-**14b**, in opposite diastereomer ratio. The mean value from the (*S*)- and (*R*)-series should eliminate the effect of mutual kinetic resolution[27] (83:17 for method A and 11:89 for method B) and, thus, match with the enantiomer ratio in **14a** and *ent*-**14a** (87.5:12.5; 75% *ee*), respectively. This is clearly not observed for method A and we assume that (-)-sparteine, which here is still present in the reaction mixture causes a further chiral interference.



(*S*)-**12b** **14b** *ent*-**14c**

method A, via (*S*)-**11** :	20 %*)	96	:	4
" , via *rac*-**11**:		53	:	47
method B, with (-)-**4a**:	78 %	14	:	86

(*R*)-**12b** **14c** *ent*-**14b**

method A, via (*S*)-**11** :	40%*)	70	:	30
method B, with (-)-**4a**:	81%	8	:	92

Scheme 6

*) yield based on *rac*-**1**,used in excess.

The stannanes **4/5** are valuable stable chiral homoenolate reagents which do not require the use of

strong bases for their activation. Further, either by following method A or B, both enantiomers of homoaldol adducts can be approached by utilizing the same enantiomerically enriched precursor **3**.

Conclusion. The stereochemistry of some synthetically important transmetallations in several chiral metal derivatives, which are easily obtained via the enantiomerically enriched lithium (-)-sparteine complex (*S*)-**3**/(-)-**2**, prepared from (*E*)-1-methyl-2-butenyl *N,N*-diisopropylcarbamate *rac*-**1** was investigated. The reaction of (*S*)-**3**/(-)-**2** and also of the diamine complexes (*S*)-**3**/TMEDA, (*S*)- and (*R*)-**9**/TMEDA, generated from optically active precursors by stereospecific deprotonation with trialkyltin halides takes place in an *anti*-S_E' reaction leading to the stannanes (*R,Z*)-(-)-**4**, accompanied by few (*S,E*)-(+)-**5**. The results are in good agreement with those obtained by Marshall[8] in the trans-stannylation of 1-(alkoxymethoxy)allyl-stannanes. Unlike the appropriate TMEDA complexes, (*S*)-**3**/(-)-**2** undergoes metal exchange by means of tetra(isopropoxy)titanium with stereoinversion. The reaction of the γ-carbamoyloxy-allylstannanes **4** with titanium tetrachloride is also an *anti*-S_E' process, in contrary to the lithio-destannylation, proceeding as *syn*-S_E' substitution.

For a working hypothesis we conclude that, like for allylsilanes[20], antarafacial processes are preferred in the electrophilic substitution reactions of the metallo-allyl carbamates if no strong bonding interaction between the cation and the electophilic reagent contributes significantly to the activation energy. The stereochemistry of the carboxylation of (*S*)-**3**/(-)-**2** is reported in the subsequent paper. The stereodivergency achieved with different reagents is advantageously utilized in generating homoenolate reagents of both enantiomeric series from the same intermediate.

EXPERIMENTAL

All organometallic reactions were performed under argon at -78°C with exclusion of air and moisture. Pentane and diethyl ether were distilled over $LiAlH_4$; (-)-sparteine [(-)-**2**] and TMEDA were dried over CaH_2 prior to use. Tetra(isopropoxy)titanium (TIPT) was used after distillation under argon. LC separations were carried out at 1-3 bar on "Silica Woelm 32-63" (Woelm Pharma GmbH & Co, Eschwege). Optical rotations of compounds **4** see Table 1. *ee*-Values were detected by conversion of γ-stannanes **4**/**5** into homoaldol adductes. All new compounds gave satisfactory elemental analyses (C,H ± 0.3%).

*Enantioselective deprotonation of rac-(E)-1-methyl-2-butenyl N,N-diisopropylcarbamate (rac-**1**); (S)-**3**/(-)-**2**.* To a solution of carbamate *rac*-**1** (2.0 mmol, diluted in 10 ml pentane) and (-)-sparteine [(-)-**2**] (2.2 mmol) was added slowly a solution of *n*-BuLi (2.2 mmol; 1.6N in hexane) and stirred vigorously for 3 h. Electrophiles (2-10 mmol, diluted in 5 mL pentane) were introduced quickly with a cooled syringe. Stirring at -70°C was continued for 30 min and the reaction mixture was allowed to warm to room temperature. It was poured onto a mixture of 2N aqueous HCl (10 ml) and ether (20 ml). The aq. solution was extracted three times with ether (each 20 ml), the combined ethereal solutions were washed with aq. sat. $NaHCO_3$ (20 ml) and dried over Na_2SO_4. After evaporation of the solvent in vacuum, the residue was purified by LC (silica gel; diethyl ether/pentane).

*(1Z,3R)- and (1E,3S)-1-Methyl-3-(tri-n-butylstannyl)-1-butenyl N,N-diisopropylcarbamate [(-)-**4a** and (+)-**5a**].* The injection of 2.4 mmol *n*-tributyltin chloride to (*S*)-**3**/(-)-**2** and aqueous workup yielded 468 mg (48%) of a mixture of (-)-**4a** and (+)-**5a** in a ratio of 87:13. Pure (-)-**4a** (≥ 80% *ee*, see below) was obtained by repeated flash chromatography (E/P 1:20). Also 176 mg (41%) recovered educt (*R*)-**1** {$[\alpha]_D^{20}$ = -8.3 (c = 1.3, $CHCl_3$)} was separated with 80% *ee* (correlated by optical rotation). **4a:** R_F(1:4): 0.53; $[\alpha]_D^{20}$ = -75.0 (c = 2.0, CH_2Cl_2); 300-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.7-1.6 (m, NCH(CH_3)$_2$ and *n*-Bu); 1.257 (d,4-H_3); 1.880 (d,1-CH_3); 2.260 (dq,3-H); 3.81 and 4.07 (m,NCH); 4.974 (dq,2-H); $J_{1',2}$= 1.1 Hz; $J_{3,4}$= 7.3 Hz; $J_{2,3}$= 11.7 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$): δ = 8.81 ($SnCH_2$); 13.68 (CH_2CH_3); 18.20 (C-4); 18.32 (C-3); 19.66 (C-1'); 21.08 (C-*i*Pr); 27.52 (CH_2CH_3); 29.28 ($SnCH_2CH_2$); 46.08 (NCH); 122.45 (C-2); 139.50 (C-1);

153.11 (C=O); $^3J_{C1',2H}$= 3.3 Hz; **5a:** R_F(1:4): 0.53; 300-MHz ^{1}H-NMR ($CDCl_3$) (mixture): δ = 0.7-1.6 (m, NCH(CH_3)$_2$ and *n*-Bu); 1.307 (d,4-H_3); 1.850 (d,1-CH_3); 2.142 (dq,3-H); 3.81 and 4.07 (m,NCH); 5.163 (dq,2-H); $J_{1',2}$= 1.1 Hz; $J_{3,4}$= 7.3 Hz; $J_{2,3}$= 12.1 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$) (mixture): δ = 8.89 ($SnCH_2$); 13.63 (CH_2CH_3); 15,85 (C-1'); 18.72 (C-3); 18.99 (C-4); 21.08 (C-*i*Pr); 27.52 (CH_2CH_3); 29.28 ($SnCH_2CH_2$); 46.08 (NCH); 122.99 (C-2); 139.71 (C-1); 153.11 (C=O); $^3J_{C1',2H}$= 6.0 Hz. $C_{24}H_{49}O_2NSn$; calc. C 57.38 H 9.83; found C 57.53 H 9.93.

(1Z,3R)- and (1E,3S)-1-Methyl-3-trimethylstannyl-1-butenyl N,N-diisopropylcarbamate [(-)-**4b** *and* (+)-**5b**]. Addition of 4.5 mmol trimethyltin chloride to *(S)*-3/(-)-**2** afforded 133 mg (35%) of a mixture of (-)-**4b** and (+)-**5b** (92:8) with 60% *ee*, besides 153 mg (36%) educt *(R)*-**1** {$[\alpha]_D^{20}$ = -2.1 (c = 1.0, $CHCl_3$)} with 20% *ee*. (-)-**4b:** R_F(1:4): 0.49; $[\alpha]_D^{20}$ = -87 (c = 1.2, CH_2Cl_2); 300-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.051 (s,Sn(CH_3)$_3$; 1.23 (d,NCH(CH_3)$_2$); 1.232 (d,4-H_3); 1.897 (d,1-CH_3); 2.206 (dq,3-H); 3.79 and 4.06 (m,NCH); 4.902 (dq,2-H); J_{iPr}= 6.8 Hz; $J_{1',2}$= 1.4 Hz; $J_{3,4}$= 7.3 Hz; $J_{2,3}$= 11.4 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$): δ = -10.76 [Sn(CH_3)$_3$]; 17.73 (C-4); 18.17 (C-3); 19.60 (C-1'); 21.07 (C-*i*Pr); 46.05 (NCH); 121.92 (C-2); 139.90 (C-1); 153.04 (C=O); $^3J_{C1',2H}$= 3.6 Hz; **5b:** 300-MHz ^{1}H-NMR ($CDCl_3$) (mixture): δ = 0.091 (s,Sn(CH_3)$_3$; 1.23 (d,NCH(CH_3)$_2$); 1.278 (d,4-H_3); 1.829 (d,1-CH_3); 2.073 (dq,3-H); 3.79 and 4.07 (m,NCH); 5.112 (dq,2-H); J_{iPr}= 6.8 Hz; $J_{1',2}$= 1.1 Hz; $J_{3,4}$= 7.3 Hz; $J_{2,3}$= 11.8 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$) (mixture): δ = -10.87 [Sn(CH_3)$_3$]; 15.91 (C-1'); 17.95 (C-4); 18.92 (C-3); 21.07 (C-*i*Pr); 46.09 (NCH); 122.44 (C-2); 140.19 (C-1); 154.38 (C=O); $^3J_{C1',2H}$= 6.5 Hz. $C_{15}H_{31}O_2NSn$; calc. C 47.90 H 8.31; found C 48.16 H 8.25.

*Deprotonation of (R)-***1**; *(1E)-1-methyl-1-trimethylstannyl-2-butenyl N,N-diisopropylcarbamate (E)-***10b**, *and (1Z,3S)-***4b**. Carbamate *(R)-***1** (1.0 mmol; 90% *ee*) was deprotonated with TMEDA/*sec*-BuLi (1.1 mmol, 1.4N in cyclohexane/isopentane). Addition of trimethyltin chloride yielded 196 mg (52%) of (+)-**4b** {$[\alpha]_D^{20}$ = +133 (c = 1.68, $CHCl_3$)}, besides 27 mg (7%) of **10b**. *(E)-***10b**: R_F(1:4): 0.68; 60-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.17 (s,$SnMe_3$); 1.33 (d,NiPr); 1.62 (s,1-CH_3); 1.83 (dd,4-H_3); 3.97 (m,NCH); 5.30-5.97 (m,3-H and 2-H); J_{iPr}= 6.8 Hz. $C_{15}H_{31}O_2NSn$; calc. C 47.90 H 8.31; found C 48.20 H 8.23.

*Deprotonation of the (Z)-1-methyl-2-butenyl carbamate rac-***8**; *rac-(1Z)-1-methyl-1-tributylstannyl-2-butenyl N,N-diisopropylcarbamate* (*rac-***10a**), *and rac-(1Z)- and rac-(1E)-1-methyl-3-tributylstannyl-1-butenyl N,N-diisopropylcarbamates* (*rac-***4a** *and rac-***5a**). To a solution of carbamate *rac-***8** (10 mmol, diluted in 20 ml pentane) and TMEDA (11 mmol) a solution of *sec*-BuLi (11 mmol, 1.4N in cyclohexane/isopentane) was added slowly and the mixture was stirred vigorously for 1 h. Tributyltin chloride (11 mmol) was added. Aqueous workup and chromatographic separation (E/P 1:10) yielded 294 mg (5%) *rac-***10a** and 3.159 g (63%) of a mixture of *rac-***4a** and *rac-***5a** in a ratio of 95:5. *rac-***10a:** R_F(1:8): 0.67; 300-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.85-1.55 (m, NCH(CH_3)$_2$ and *n*-Bu); 1.597 (s,1-CH_3); 1.654 (dd,4-H_3); 3.90 (m,NCH); 5.174 (dq,3-H); 5.507 (dq,2-H); $J_{2,3}$= 11.9 Hz; $J_{3,4}$= 7.2 Hz; $J_{2,4}$= 1.6 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$): δ = 12.44 ($SnCH_2$); 13.72 (CH_2CH_3); 14.44 (C-4); 20.83 and 21.37 (C-*i*Pr); 26.43 (C-1'); 27.75 (CH_2CH_3); 29.30 ($SnCH_2CH_2$); 45.68 (NCH); 79.65 (C-1); 118.32 (C-3); 137.39 (C-2); 155.71 (C=O). $C_{24}H_{49}O_2SnN$; calc. C 57.38 H 9.83; found C 57.36 H 9.91.

Deprotonation of (1R,2Z)-1-methyl-2-butenyl N,N-diisopropylcarbamate [*(R)-***8**]; *(R,Z)-*(-)-**4a**, *(S,E)-*(+)-**5a**, *and (-)-***10a**. Described deprotonation of 4.0 mmol of carbamate *(R)-***8** (100% *ee*) and stannylation with tributyltin chloride afforded 1.113 g (55%) of a mixture (95:5) of *(R,Z)-*(-)-**4a** {$[\alpha]_D^{20}$ = -101 (c = 1.2, CH_2Cl_2)} and *(S,E)-*(+)-**5a**, besides 139 mg (7%) of *(Z)-***10a**.

Deprotonation of (1S,2Z)-1-methyl-2-butenyl N,N-diisopropylcarbamate [*(S)-***8**]; *(S,Z)-*(+)-**4a**, *(R,E)-*(-)-**5a** *and (+)-***10a**. Described deprotonation of 9.9 mmol of carbamate *(S)-***8** (100% *ee*) and stannylation with tributyltin chloride afforded 2.738 g (53%) of a mixture (95:5) of *(S,Z)-*(+)-**4a** {$[\alpha]_D^{20}$ = +101 (c = 1.1,

CH_2Cl_2)}and *(R,E)*-(-)-**5a**, besides 294 mg (6%) α-adduct **10a**.

Deprotonation of (1R,2Z)-1-methyl-2-butenyl N,N-diisopropylcarbamate [*(R)*-**8**]; *(R,Z)*-(-)-**4b**, *(S,E)*-(+)-**5b** *and (Z)*-**10b**. The described deprotonation of 4.1 mmol of carbamate *(R)*-**8** (100% *ee*) and stannylation with 4.5 mmol trimethyltin chloride yielded 1.00 g (65%) of a mixture (90:10) of *(R,Z)*-**4b** {$[\alpha]_D^{20}$ = -127.4 (c = 1.36,$CHCl_3$)} and *(S,E)*-**5b**, besides 92 mg (6%) **10b**. *(Z)*-**10b**: R_F(1:4): 0.68; 300-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.088 [s,$Sn(CH_3)_3$]; 1.21 (d,NiPr); 1.594 (s,1-CH_3); 1.638 (dd,4-H_3); 3.79 and 4.05 (m,NCH); 5.245 (dq,3-H); 5.531 (dq,2-H); J_{iPr}= 6.9 Hz; $J_{2,3}$= 11.7 Hz; $J_{3,4}$= 7.2 Hz; $J_{2,4}$= 1.7 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$): δ = -6.41 ($SnCH_3$); 14.54 (C-4); 20.82 and 21.38 (C-*i*Pr); 25.67 (C-1'); 45.49 and 46.03 (NCH); 78.46 (C-1); 119.26 (C-2); 137.53 (C-3); 156.10 (C=O). $C_{15}H_{31}O_2NSn$; calc. C 47.90 H 8.31; found C 47.97 H 8.08.

Deprotonation of (1S,2Z)-1-methyl-2-butenyl N,N-diisopropylcarbamate [*(S)*-**8**]; *(S,Z)*-(+)-**4b**, *(R,E)*-(-)-**5b** *and (+)*-**10b**. The described deprotonation of 1.01 mmol of carbamate *(S)*-**8** (100% *ee*) and stannylation with 1.1 mmol trimethyltin chloride afforded 229 mg (61%) of a mixture (90:10) of *(S,Z)*-(+)-**4b** {$[\alpha]_D^{20}$ = +138 (c = 3, $CHCl_3$)} and *(R,E)*-(-)-**5b**, besides 23 mg (6%) of α-adduct **10b**.

*Lithiodestannylation of (1Z,3R)-(-)-***4b** *to (1Z,3R)-***7** *and restannylation to (1Z,3S)-(+)-***4b**. 1 mmol of *(1Z,3R)*-(-)-**4b** {$[\alpha]_D^{20}$ = -127 (c = 1.4, $CHCl_3$; 95% *ee*} was dissolved in 10 ml of diethyl ether and treated at -78°C with a mixture of 1 mmol 1,2-dimethoxyethane and 1.4 mmol of a *sec*-BuLi solution (1.1N in hexane/isopentane). After 6 min the educt was consumed (DC-control) and 2.0 mmol of trimethyltin chloride was added, and followed by aq. workup as described above. Besides a small amount of **5b**, the reaction afforded 204 mg (54%) of *(3S,1Z)*-(+)-**4b** with $[\alpha]_D^{20}$ = +67.0 (CH_2Cl_2); according to an overall chirality transfer of 61%.

*Reaction of (S)-***3***/*(-)-**2** *with TIPT and subsequent homoaldol reaction with aldehydes; general procedure.* To a solution of *(S)*-**3**/(-)-**2** [2 mmol, prepared from *rac*-**1** and each 1.1 equiv. of (-)-sparteine [(-)-**2**] and *n*-BuLi (1.6N in hexane)] TIPT (4 equiv.) was introduced with a syringe. Stirring at -70°C was continued for 30 min and the aldehyde (2 equiv.) was added slowly. The reaction mixture was allowed to warm to room temperature and it was poured onto a mixture of 2N aq. HCl (10 ml) and ether (20 ml). The aqueous solution was extracted three times with ether (each 20 ml), the combined ethereal solutions were washed with aq. sat. $NaHCO_3$ (20 ml) and dried over Na_2SO_4. After evaporation of the solvent in vacuum, the residue was purified by LC (silica gel; diethyl ether/pentane 1:4).

Reaction with 2-methylpropanal; (1Z,3R,4S)-(4-hydroxy-1,3,5-trimethyl-1-hexenyl) N,N-diisopropylcarbamate (**14a**). Deprotonation of 2 mmol *rac*-**1** over 3 h, addition of 6.0 mmol TIPT at -78°C, stirring for 30 min and addition of 3 mmol 2-methylpropanal yields 102 mg (36%) **14a** with 75% *ee*. The enantiomeric excess of compound **14a** was determined by 90-MHz ^{1}H-NMR spectroscopy with 10 mol% tris[(3-heptafluoropropylhydroxymethylene)-d-camphorato]europium(III), [Eu(hfc)$_3$]. Also 319 mg (56%) of educt *(R)*-**1** {$[\alpha]_D^{20}$ = -1.2 (c = 1.8, $CHCl_3$)} was recovered. **14a:** $[\alpha]_D^{20}$ = -5.2 (c =1.3, MeOH); R_F(1:1): 0.32; 300-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.838 (d,6-H_3); 0.952 (d,5-CH_3); 1.083 (d,3-CH_3); 1.167-1.372 (m,iPr); 1.762 (dqq,5-H); 1.915 (d,1-CH_3); 2.464 (ddq,3-H); 2.821 (br., OH); 3.104 (dd,4-H); 3.825 and 4.143 (m,NCH); 4.958 (dd,2-H); $J_{1,1'}$= 1.1 Hz; $J_{2,3}$= 10.3 Hz; $J_{3,3'}$= 6.8 Hz; $J_{3,4}$= 8.5 Hz; $J_{4,5}$= 3.4 Hz; $J_{5,5'}$= 6.8 Hz; $J_{5,6}$= 6.8 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$): δ = 14.49 (C-3'); 17.27 (C-6); 19.75 (C-5'); 20.21 (C-1'); 20.29 and 21.40 (C-iPr); 26.83 (C-5); 34.49 (C-3); 45.35 and 47.15 (NCH); 79.24 (C-4); 120.09 (C-2); 145.58 (C-1); 154.89 (C=O). $C_{16}H_{31}O_3N$; calc. 67.33 H 10.95; found 67.20 H 10.90.

*Reaction of rac-***1** *with (S)-2-(tert-butyldimethylsilyloxy)propanal [(S)-***12b***]; (1Z,3R,4R,5S)- and (1Z,3S,4S,5S)-N,N-(5-tert-butyldimethylsilyloxy-4-hydroxy-1,3-dimethyl-1-hexenyl) N,N-diisopropylcarb-*

amate (**14b** *and ent*-**14c**). 25.0 mmol *rac*-**1**, 29 mmol TMEDA, 27.5 mmol TIPT, and 27.5 mmol (*S*)-**12** afforded 3.51 g (35%) *ent*-**14c** and 4.01 g (40%) **14b**. The diastereomeric ratio (47:53) was also detected by GC (220°C, R_t(**4b**): 4.6 min.; R_t(**4c**): 4.2 min.). **14b:** R_F(1:1): 0.44; $[\alpha]_D^{20}$ = -5.6 (c = 1.2, MeOH); 300-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.052 (s,Si-CH_3); 0.874 (s,*t*Bu-H_3); 0.938 (d,3-CH_3); 1.071 (d,6-H_3); 1.23 (m,iPr); 1.886 (d,1-CH_3); 2.397 (ddq,3-H); 2.66 (s,br.,OH); 3.284 (dd,4-H); 3.848 (dq,5-H); 3.83 and 4.07 (m,NCH); 4.975 (dq,2-H); $J_{1',2}$= 1.1 Hz; $J_{2,3}$= 9.6 Hz; $J_{3,3'}$= 6.8 Hz; $J_{3,4}$= 8.5 Hz; $J_{4,5}$= 3.3 Hz; $J_{5,6}$= 6.2 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$): δ = -4.79 and -4.53 (CH_3-Si); 16.49 (C-6); 17.13 (C-3'); 18.05 (SiC); 20.08 (C-1'); 20.46 and 21.43 (C-iPr); 25.81 (Si*C*CH_3); 33.47 (C-3); 45.70 and 46.59 (NCH); 69.96 (C-5); 78.62 (C-4); 119.45 (C-2); 145.24 (C-1); 153.46 (C=O). $C_{21}H_{43}O_4NSi$; calc. C 62.79 H 10.79; found C 62.90 H 10.80.

ent-**14c:** R_F(1:1): 0.58; $[\alpha]_D^{20}$ = +6.5 (c = 1.2, MeOH); 300-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.080 (s,Si-CH_3); 0.883 (s,*t*Bu-H_3); 1.058 (d,3-CH_3); 1.098 (d,6-H_3); 1.235 (m,iPr); 1.884 (d,1-CH_3); 2.529 (ddq,3-H); 2.82 (s,br.,OH); 3.128 (dd,4-H); 3.760 (dq,5-H); 3.80 and 4.05 (m,NCH); 5.027 (dq,2-H); $J_{1',2}$= 1.1 Hz; $J_{2,3}$= 9.9 Hz; $J_{3,3'}$= 6.9 Hz; $J_{3,4}$= 4.9 Hz; $J_{4,5}$= 6.1 Hz; $J_{5,6}$= 6.1 Hz; 75.5-MHz ^{13}C-NMR ($CDCl_3$): δ = -4.82 and -4.11 (CH_3-Si); 18.01 (SiC); 18.14 (C-3'); 19.75 (C-6); 19.89 (C-1'); 20.45 and 21.33 (C-iPr); 25.86 (Si*C*CH_3); 32.53 (C-3); 45.96 (NCH); 70.20 (C-5); 79.29 (C-4); 117.95 (C-2); 145.09 (C-1); 153.14 (C=O). $C_{21}H_{43}O_4NSi$; calc. C 62.79 H 10.79; found C 62.93 H 10.70.

*Reaction with (R)-2-(tert-butyldimethylsilyloxy)propanal [(R)-***12b***]; (1Z,3R,4R,5R)- and (1Z,3S,4S,5R)-N,N-(5-tert-butyldimethylsilyloxy-4-hydroxy-1,3-dimethyl-1-hexenyl) N,N-diisopropylcarbamate* (**14c** *and ent*-**14b**). The solution of *(S)*-**3**/(-)-**2** [0.5 mmol, prepared from *rac*-**1**] was quenched with 1.0 mmol TIPT followed by 0.32 mmol *(R)*-**12b** and yielded 41 mg (40%) of a mixture of *ent*-**14b** and **14c** in a 30:70 ratio (GC-analysis).

*Reaction with (S)-2-(tert-butyldimethylsilyloxy)propanal [(S)-***12b***]; (1Z,3R,4R,5S)- and (1Z,3S,4S,5S)-N,N-(5-tert-butyldimethylsilyloxy-4-hydroxy-1,3-dimethyl-1-hexenyl) N,N-diisopropylcarbamate* (**14b** *and ent*-**14c**). The solution of *(S)*-**3**/(-)-**2** [1.0 mmol, prepared from *rac*-**1**] was quenched with 2.0 mmol TIPT and reaction with 0.53 mmol *(S)*-**12b** afforded 80 mg (20%) of a mixture of **14b** and *ent*-**14c**. The products were not separated; GC-analysis afforded a diastereomeric ratio of 96:4.

*Titanio-destannylation of (-)-***4a***/(+)-***5a** *and homoaldol reaction with aldehydes, general procedure.* To a stirred solution of equimolar amounts of aldehyde and stannane *(-)*-**4a**/*(+)*-**5a** (as prepared from *rac*-**1** by the sparteine method) in dichloromethane (1 ml/ 0.1 mmol) at -78°C, 1.2 equiv. of titanium tetrachloride (1N solution in hexane) was added slowly. After 30 min, the mixture was allowed to warm to room temperature and it was poured onto a mixture of 2N aq. HCl (10 ml) and ether (20 ml). The aq. phase was extracted three times with ether (each 20 ml), the combined ethereal solutions were washed with aq. sat. $NaHCO_3$ (20 ml) and dried over Na_2SO_4. After evaporation of the solvent in vacuum, the residue was purified by LC (silica gel; diethyl ether/pentane 1:4).

*Reaction with 2-methylpropanal; ent-*14a. By use of 0.4 mmol *(-)*-**4a**/*(+)*-**5a** (as prepared from *rac*-**1** by the sparteine method) and 0.4 mmol 2-methylpropanal, the reaction afforded 84 mg (74%) of *ent*-**14a** with 80% *ee* (^{1}H-NMR shift experiment).

*Reaction with [(S)-***12b***]; ent-***14c** *and* **14b**. By use of 0.16 mmol *(-)*-**4a**/*(+)*-**5a** and 0.16 mmol *(S)*-**12b**, the reaction afforded 50 mg (78%) of a mixture of *ent*-**14c** and **14b** in a ratio of 86:14 (GC).

*Reaction with [(R)-***12b***]; ent-***14b** *and* **14c**. By use of 0.16 mmol *(-)*-**4a**/*(+)*-**5a** and 0.16 mmol *(R)*-**12b**, the reaction yielded 52 mg (81%) of a mixture of *ent*-**14b** and **14c** in a ratio of 92:8 (GC).

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