rogenase substrates. The results of these investigations will be reported subsequently.

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Supplementary Material Available: Crystal structure data for $(Et_4N)_5[Mo_2Fe_6S_8(SPh)_9]$: unit-weighted least-squares planes for the anion (Table S-I), positional and thermal parameters for benzenethiolate carbon atoms (Table S-II) and cation carbon and nitrogen atoms (Table S-III), and values of $10|F_o|$ and $10|F_c|$ (Table S-IV) (47 pages). Ordering information is given on any current masthead page.

Reaction of Trimethyl- and Triphenylstannate, $(CH_3)_3Sn^-$ and Ph_3Sn^-, with Optically Active 2-Octyl Bromide, Chloride, and Tosylate[1]

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Abstract: The reaction of lithium, sodium, and potassium trimethylstannate, $(CH_3)_3SnLi$, -Na, and -K, and triphenylstannate, Ph_3SnLi, -Na, and -K, with optically active 2-octyl tosylate, chloride, and bromide is reported. Alkylation of $(CH_3)_3SnM$ with 2-octyl tosylate proceeds with complete inversion at carbon. The corresponding reactions with 2-octyl chloride and especially 2-octyl bromide show considerably greater variations in reaction stereoselectivity. These variations depend on a variety of reaction parameters, including the order of reagent addition, i.e., normal vs. inverse addition of reagents, reaction temperature, solvent, gegenion, concentration, and additives. Thus, for example, at 0 °C the normal addition reaction of 2-octyl chloride with $(CH_3)_3SnM$ in THF proceeds with 100% inversion of configuration, while the equivalent reactions with 2-octyl bromide proceed with 34% (M = Na), 33% (M = K), and 53% (M = Li) *net* inversion. The latter reactions are more stereoselective when carried out at lower temperatures: at −70 °C the corresponding values are 62% (M = Na) and 83% (M = Li) *net* inversion. Stereoselectivity in these reactions is dramatically influenced by the order of reagent addition. Thus, under inverse-addition conditions, for example, the reaction of $(CH_3)_3SnM$ with 2-octyl bromide in THF at 0 °C occurs with high stereoselectivity (97% and 98% net inversion, respectively, for M = Li and Na) and with minor adjustment of other parameters can be made to occur stereospecifically. Both the normal and the indirect addition of Ph_3SnLi and -Na to 2-octyl bromide occur with complete inversion of configuration at carbon. A comparison of the reactivity of $(CH_3)_3SnM$ and Ph_3SnM reveals that the latter is significantly less reactive than the former; triphenylstannate, however, is the more stereoselective reagent, its reaction with optically active 2-bromooctane being essentially stereospecific, irrespective of the order of reagent addition. The results of this study and those from earlier investigations involving the *cis*- and *trans*-4-*tert*-butylcyclohexyl and cyclopropylcarbinyl systems are compared and discussed as well as the reliability of recently reported trapping experiments for discerning between the S_N2 and free radical components of such reactions.

In earlier reports we presented the results of our investigations of the reaction of selected metalate anions with various alkyl halides.[2] These studies revealed, inter alia, that the course of these reactions varies substantially with the nature of the leaving group. Thus, for example, *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylates react with Me_3SnLi in THF at 0 °C to afford, respectively, *trans*- and *cis*-(4-*tert*-butylcyclohexyl)trimethyltin corresponding to complete inversion of configuration at carbon. By comparison, the corresponding reaction with *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide produces a mixture of these products exhibiting essentially complete loss of stereochemical integrity.

As a stereochemical probe, the 4-*tert*-butylcyclohexyl system suffers from certain limitations which do not attend the use of an optically active substrate. We report here the results of our investigation of the reaction of optically active 2-octyl tosylate, chloride, and bromide with $(CH_3)_3SnM$ and Ph_3SnM, along with several related findings.

Results

Preparation of Optically Pure 2-Octyltrimethyltin and 2-Octyltriphenyltin. In order to employ traditional experimental procedures (i.e., polarimetry), it was necessary to establish the absolute rotation of optically active 2-octyltrimethyltin, **1**. The fact that the optical resolution of such a substance is impractical requires that a stereospecific synthesis of **1** be available. On the basis of our previous observation that the reaction of $(CH_3)_3SnLi$ with both *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylate proceeds with essentially complete (>99%) inversion of configuration,[2] it seemed reasonable to expect that the corresponding reaction with the tosylate of optically active 2-octanol would occur with equivalent stereochemical integrity. As seen below, the reaction of lithium trimethylstannate with the tosylate of (−)-(*R*)-2-octanol does yield optically active **1**. Of course, this result does not establish that the observed rotation is the maximum value. We attempted to establish this fact by carrying out the equivalent synthesis by an independent route.

$$(-)\text{-}(R)\text{-}2\text{-}C_8H_{17}OH \xrightarrow[py]{TsCl} (-)\text{-}(R)\text{-}2\text{-}C_8H_{17}OTs \quad (1)$$

$$(-)\text{-}(R)\text{-}2\text{-}C_8H_{17}OTs + (CH_3)_3SnLi \xrightarrow[-78\ °C]{THF} (+)\text{-}(S)\text{-}2\text{-}C_8H_{17}Sn(CH_3)_3 \quad (2)$$

(*S*)-1, $[\alpha]^{25}_D$ + 26.1° (neat)

Lithium diorganocuprates have been extensively employed as reagents for the production of carbon–carbon σ bonds by reaction

(1) Supported by the National Science Foundation, Grant 80-17405, and DOE, Contract DE-AS05-80ER-1062.

(2) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

0002-7863/82/1504-2831$01.25/0

Table I. Normal-Addition Reaction of $(CH_3)_3SnM$ with Optically Active 2-Octyl Bromide, Chloride, and Tosylate

$$(CH_3)_3SnCl \xrightarrow{M} (CH_3)_3SnM \xrightarrow{R^*-X} (CH_3)_3SnR^* + MX$$

R*-X,[a] $[\alpha]_D^{25}$ (deg)	$(CH_3)_3SnM$ (concn, M)	temp, °C	solvent	% yield of R*-$Sn(CH_3)_3$	$[\alpha]_D^{25}$, deg obsd	$[\alpha]_D^{25}$, deg corr[b]	entantiomeric excess,[c] %
Br, +39.6	Li (0.2)	0	THF	74	−11.6	−12.7	49
+39.6	(0.4)	0	THF	69	−12.6	−13.8	53
+39.6	(0.8)	0	THF	74	−9.49	−10.4	40
+35.5	(0.4)	−70	THF	60	−17.6	−21.5	82
+35.5	Na (0.2)	0	THF	66	−7.01	−8.57	33
+35.5	(0.4)	0	THF	55	−7.25	−8.86	34
+35.5	(0.8)	0	THF	32	−7.79	−9.52	36
+35.5	(0.4)	−70	THF	45	−13.2	−16.1	62
+34.8	K (0.2)	0	THF	80	−6.96	−8.68	33
+35.5	(0.4)	0	THF	54	−6.90	−8.44	33
+32.3	(0.8)	0	THF	66	−8.10	−10.9	42
OTs, −8.88[b]	Li (0.4)	0	THF	20	+23.0	+25.6	98
−8.90[b]	(0.4)	−70	THF	4	+23.5	+26.1	100
Cl, +6.85	Li (0.4)	25	THF	51	−4.32	−23.5	90
+34.4	(0.4)	0	THF	62	−24.2	−26.2	100
Br, +34.9	(0.4)	0	DME	79	−7.19	−8.94	34
+37.3	Na (0.4)	0	DME	56	−6.96	−8.10	31
+37.3	K (0.4)	0	DME	52	−7.23	−8.41	32

[a] R = 2-octyl; rotations of optically pure (+)-(*S*)-2-halooctane: $[\alpha]_D^{20}$ +37.3° (Cl), $[\alpha]_D^{20}$ +43.4° (Br); see ref 16. Rotation of optically pure (−)-(*R*)-2-octanol: $[\alpha]_D^{17}$ −9.90°; see ref 16. [b] Specific rotation of the corresponding (−)-(*R*)-2-octanol. [c] Based on a value for the rotation of optically pure 1 of 26.1 °C; see text for discussion.

with alkyl halides and tosylates.[3] These reactions have been demonstrated to proceed with the high stereoselectivity usually associated with an S_N2 displacement at carbon.[4] In the hope of extending this stereoselectivity to the formation of carbon–tin bonds, we examined the reaction of "$[(CH_3)_3Sn]_2CuLi$" with optically active 2-bromooctane.[5a] We feel that the results, summarized below, sustain our contention that the value 26.1° represents the maximum rotation for optically active 2-octyltrimethyltin.[5b]

$$(CH_3)_3SnLi \xrightarrow[THF,\ -78\ °C]{CuI} \text{"}[(CH_3)_3Sn]_2CuLi\text{"} \qquad (3)$$

$$\text{"}[(CH_3)_3Sn]_2CuLi\text{"} + (+)\text{-}(S)\text{-}2\text{-}C_8H_{17}Br \xrightarrow[-70\ °C]{THF} (-)\text{-}(R)\text{-}2\text{-}C_8H_{17}Sn(CH_3)_3 \quad (4)$$
$$(R)\text{-}\mathbf{1},\ [\alpha]^{25}_D\ -26.1°\ (\text{neat})$$

In a parallel study, the reaction of lithium triphenylstannate with the tosylate of optically active 2-octanol was also examined. Previous investigations indicated a high degree of stereoselectivity in the reaction of Ph_3SnNa with optically active *sec*-butyl halides.[6] In light of this fact and the stereospecificity exhibited in the reactions of $(CH_3)_3Sn^-$ with various alkyl tosylates, we conclude that the value of 23.3° (*c* 4.15 in benzene) to be the maximum rotation of 2-octyltriphenyltin, **2**.[7]

$$(-)\text{-}(R)\text{-}2\text{-}C_8H_{17}OTs \xrightarrow[THF,\ 25\ °C]{Ph_3SnLi} (+)\text{-}(S)\text{-}2\text{-}C_8H_{17}SnPh_3$$
$$(S)\text{-}\mathbf{2},\ [\alpha]^{25}_D\ +23.3°\ (c\ 4.15,\ C_6H_6)$$

The Normal-Addition Reaction of $(CH_3)_3SnM$ with Selected Alkyl Halides. The reaction of $(CH_3)_3SnM$, prepared from $(CH_3)_3SnCl$, with (+)-(*S*)-2-bromooctane under normal-addition conditions, i.e., addition of alkyl halide to $(CH_3)_3SnM$, is summarized in Table I and II. Several aspects of these data are noteworthy. First, it is apparent that the nature of the leaving group has a significant influence on the degree of stereoselectivity, the observed order being OTs ≳ Cl > Br. Second, greater stereoselectivity is observed with $(CH_3)_3SnLi$ (~50% net *inversion*, X = Br) than with $(CH_3)_3SnNa$ and -K (~33% net *inversion*, X = Br). Third, regardless of gegenion, temperature has a pronounced *inverse* effect on the stereoselectivity. Fourth, stereoselectivity is diminished in DME relative to THF for $(CH_3)_3SnLi$ but remains essentially unchanged for $(CH_3)_3SnNa$ and -K. Fifth, stereoselectivity is unaffected by the concentration of $(CH_3)_3SnM$ within the range 0.2–0.4 M; however, at a concentration 0.8 M, alkylation of $(CH_3)_3SnLi$ becomes somewhat less stereoselective while that of $(CH_3)_3SnNa$ and -K exhibits somewhat greater stereoselectivity. Sixth, the stereoselectivity of these reactions displays an unexpected sensitivity to the procedure employed to prepare $(CH_3)_3SnM$. Thus, reaction of optically active 2-bromooctane with halide-free $(CH_3)_3SnNa$ and -K, prepared by reduction of hexamethylditin (Table II), exhibits

(3) Schwartz, R. H.; San Filippo, J., Jr. *J. Org. Chem.* **1979**, *44*, 2705 and references therein.

(4) (a) Whiteside, G. M.; Fischer, W.F., Jr.; San Filippo, J., Jr.; Basche, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. (b) Johnson, C. R., Dutra, G. A. *Ibid.* **1973**, *95*, 7783 and references therein.

(5) (a) For an earlier study of the reactions of "$[(CH_3)_3Sn]_2CuLi$", see: Hudec, J. *J. Chem. Soc., Perkin Trans.* **1975**, 1020. (b) The value of 26.1° observed for optically pure (neat) 2-octyltrimethyltin is essentially the same as the previously observed rotation of 26° reported for optically pure (neat) 2-butyltrimethyltin prepared by asymmetric induction, see: Rahm, A.; Pereyre, M. *J. Organomet. Chem.* **1977**, *139*, 49.

(6) Jensen, F. R.; Davis, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 4047. However, these results have been questioned (ref 27).

(7) Attempts to prepare 2-octyltriphenyltin by reaction of "$[Ph_3Sn]_2CuLi$" with 2-octyl bromide were largely unsuccessful; this failure appeared to be a consequence of the relative instability of the purported species "$[Ph_3Sn]_2CuLi$" under the reaction conditions.

(8) Bangerter, B. W.; Beatty, R. P.; Kouba, J. K.; Wreford, S. S. *J. Org. Chem.* **1977**, *42*, 3247.

(9) Smith, G. F.; Kuivila, H. F.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. Alnajjar, M. S.; Kuivila, H. G. *J. Org. Chem.* **1981**, *44*, 1053. Kuivila, H. G.; Smith, G. F. *Ibid.* **1980**, *45*, 2919.

(10) It is, of course, well-known that the degree of association of organolithium reagents is strongly solvent dependent: Wakefield, B. J. "The Chemistry of Organolithium Compounds", Pergamon Press: New York, 1974; p 4. The presence of basic solvents in an organolithium reagent solution generally predisposes the aggregate toward dissociation into smaller and presumably better solvated fragments, see: Langer, A. W. *Adv. Chem. Ser.* **1974**, *No. 130*, 1. Finally, basic solvents are known to promote electron-transfer reactions: Russell, G. A.; Lamson, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 3967. Russell, G. A.; Janzen, E. G.; Strom, E. T. *Ibid.* **1964**, *86*, 1807 and references therein. For a discussion of the influence of amine additives on the mechanism on the mehcanism of another electron-transfer reaction also involving organolithium reagents, see: Panek, E. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1972**, *94*, 8768.

(11) Tables VI–VII present a comparison of the influence of normal- and inverse-addition modes on the stereoselectivity and product distribution produced by the reaction of 2-bromooctane and $(CH_3)_3SnNa$ in the presence of *tert*-butylamine and dicyclohexyylphosphine. It is clear that the presence of these additives and the order of reagent mixing can have a substantial influence on stereoselectivity and product distributions; in the absence of reliable information concerning how such additives perturb the mechanism of these reactions, it is unreasonable to speculate on the origins of these effects.

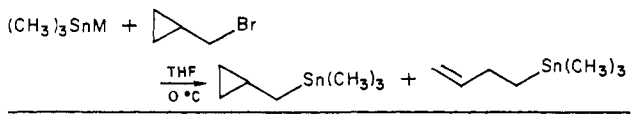
Table II. Normal-Addition Reaction of $(CH_3)_3SnM$ with Optically Active 2-Octyl Bromide and Tosylate

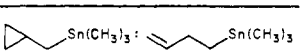
$$^1/_2(CH_3)_6Sn_2 + M \rightarrow (CH_3)_3SnM \xrightarrow[-MX]{R^*-X} (CH_3)_3SnR^*$$

R*-X,[a] $[\alpha]_D^{25}$ (deg)	Me_3SnM (concn, M)	temp, °C	solvent	% yield of R*-$Sn(CH_3)_3$	$[\alpha]_D^{25}$, deg obsd	$[\alpha]_D^{25}$, deg corr[b]	entantiomeric excess,[c] %
Br, +34.4	Li (0.2)	0	THF	84	−9.68	−12.2	47
+31.8	(0.4)	0	THF	70	−8.78	−12.0	46
+34.4	(0.8)	0	THF	76	−9.04	−11.4	44
+34.4	(0.4)	−70	THF	44	−14.3	−18.0	69
+34.4	Na (0.2)	0	THF	75	−8.61	−10.9	42
+33.2	(0.4)	0	THF	77	−8.73	−11.4	44
+34.4	(0.8)	0	THF	68	−7.86	−9.92	38
+34.4	(0.4)	−70	THF	25	−16.3	−20.6	79
+27.4	K (0.2)	0	THF	36	−7.47	−11.9	46
+33.2	(0.4)	0	THF	32	−8.21	−10.7	41
+27.4	(0.8)	0	THF	26	−5.63	−8.92	34
+38.1	Li (0.4)[d]	0	THF-Et_2O (80:20)	75	−11.4	−13.0	50
Cl, +30.1	Na (0.4)	0	THF	53	−19.4	−24.0	92
OTs, −8.87[b]	Li (0.4)	0	THF	39	+21.6	+24.1	93

[a] R = 2-octyl. [b] See ref 16. [c] Based on a value for the rotation of optically pure 1 of 26.1°; see text for discussion. [d] Prepared by reaction of CH_3Li with $(CH_3)_6Sn_2$.[25]

Table III. Influence of Alkali Halide on the Product Ratios for the Reaction



$(CH_3)_3SnM$ (concn, M)	
M = Li (0.4)[a]	39:61
Na (0.4)[a]	37:63
K (0.4)[a]	59:41
Li (0.4)[b]	83:17
Na (0.4)[b]	85:15
K (0.4)[b]	87:13
Li (0.4)[c]	38:62

[a] Prepared from $(CH_3)_6Sn_2$ and lithium, sodium, or potassium. [b] Prepared from $(CH_3)_3SnCl$ and lithium, sodium, or potassium. [c] Prepared from $(CH_3)_3SnBr$ and lithium. For a further discussion of the reaction of metalate anions with cyclopropylcarbinyl halides and tosylate, see ref 2.

Table IV. Normal- and Inverse-Addition Reaction of $(CH_3)_3SnLi$ with *cis*- and *trans*-4-*tert*-Butylcyclohexyl Bromide, 3[a]

$$(CH)_3)_3SnLi + RBr \xrightarrow[3 \quad 0\ °C]{THF} \underset{trans\text{-}4}{trans\text{-}RSn(CH_3)_3} + \underset{cis\text{-}4}{cis\text{-}RSn(CH_3)_3}$$

concn of $(CH_3)_3SnLi$, M	conformation of 3	$RSn(CH_3)_3$, trans:cis normal addition[e]	$RSn(CH_3)_3$, trans:cis inverse addition[e]
0.4[b]	cis	70:30	65:35
0.4[b]	trans	74:26	63:37
0.4[c]	cis	76:24	*f*
0.4[c]	trans	78:22	*f*
0.4[d]	cis	72:28	66:34
0.4[d]	trans	73:27	69:31

[a] Control experiments revealed that neither *trans*- nor *cis*-4 suffer any observable isomerization in the presence of $(CH_3)_3SnLi$. [b] Prepared from $(CH_3)_3SnCl$ and lithium. [c] Prepared from $(CH_3)_3SnBr$ and lithium. [d] Prepared from $(CH_3)_6Sn_2$ and lithium. [e] *cis*- and *trans*-(4-*tert*-butylcyclohexyl)trimethyltins have been previously characterized.[2] [f] Not determined.

somewhat greater stereoselectivity than the equivalent reaction employing halide-containing $(CH_3)_3SnNa$ and -K, prepared by the alkali-metal reduction of trimethyltin chloride (Table I). These effects exhibit an inverse concentration dependence such that at higher (≳0.8 M) concentrations of $(CH_3)_3SnM$, the *reverse* behavior obtains.

We have also observed that in the reaction of $(CH_3)_3SnLi$, -Na, and -K with cyclopropylcarbinyl bromide, greater rearrangement occurs with halide-free than with halide-containing $(CH_3)_3SnM$ (cf. Table III) while, by comparison, the presence or absence of alkali halide has no apparent effect on the product distribution produced by the reaction of $(CH_3)_3SnM$ with *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide (cf. Table IV). This fact suggests that the presence of metal halide is more influential in determining the initial partitioning between electron-transfer and S_N2 pathways than it is in affecting the carbon–tin bond-forming process(es).

The Inverse-Addition Reaction of $(CH_3)_3SnM$ with Selected Alkyl Halides. The stereoselectivity of the reaction of $(CH_3)_3SnM$ with 2-octyl bromide exhibits a dramatic dependence on the order of reagent mixing. Thus, slow addition of a solution of optically active 2-octyl bromide to a stirred solution of $(CH_3)_3SnNa$ in THF results in the low stereoselectivity summarized in Table I. However, inverse addition, i.e., addition of a solution of $(CH_3)_3SnNa$ to a stirred solution of (*S*)-2-octyl bromide in THF, results in a significant increase in stereoselectivity (cf. Table V). Indeed, it is seen (Table V) that with only a minor change in concentration, this reaction, which under direct addition (Table I), results in only 33% net inversion, under inverse addition conditions actually becomes stereospecific.

The order of reagent mixing also influences the course of the reaction of $(CH_3)_3SnM$ with 4-*tert*-butylcyclohexyl bromides (cf. Table IV): treatment of *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide produces a trans:cis product ratio of 64:36. By comparison, a ratio of 72:28 is observed under normal-addition procedures.[2] Thus, although stereochemical equilibration still obtains, isomer distribution is shifted toward the cis isomer. It follows that such a result is a consequence of the difference(s)—presumably largely steric in nature—between the nature of the carbon–tin bond-forming step(s) under these differing conditions.[12]

Reaction of Ph_3SnLi with Optically Active 2-Bromooctane. In a pioneering study of the preparation of optically active organo derivatives of group 4 elements, Jensen and Davis[6] reported that the reaction of Ph_3SnNa with (+)-(*S*)-2-butyl bromide in DME yields triphenyl-2-butyltin with ca. 88% *inversion* of configuration at carbon. In light of the above results, this observation, together with those of Wreford and co-workers[8] on the relative reactivity of $(CH_3)_2PM$ and Ph_2PM, suggests that some phenyl-substituted

(12) This statement is consistent with the earlier conclusion[2] that the reaction of $(CH_3)_3SnM$ with *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide occurs essentially completely by a one-electron-transfer pathway and that the resulting ratio of product isomers is determined by the nature of product-forming (C–Sn bond-forming) step; by contrast, the distribution of optical isomers produced by the reaction of $(CH_3)_3SnM$ with optical active 2-bromooctane is a reflection of the partitioning between electron-transfer and S_N2 pathways.

Table V. Inverse-Addition Reaction of $(CH_3)_3SnM$ with (+)-(*S*)-Octyl Bromide, Chloride, and Tosylate

$$(CH_3)_6Sn_2 + 2M \rightarrow 2(CH_3)_3SnM \xrightarrow[THF]{R^*-X} 2(CH_3)_3SnR^* + MX$$

R*–X,[a] $[\alpha]_D^{25}$ (deg)	Me_3SnM (concn, M)	temp, °C	% yield of $RSnMe_3$	$[\alpha]_D^{25}$, deg obsd	$[\alpha]_D^{25}$, deg corr[b]	entaniomeric excess, %
OTs, −8.89[b]	Li (0.4)	−70	8	+23.0	+25.6	98
Cl, +30.5	Na (0.4)	0	52	−19.9	−24.3	93
Br, +28.4	Li (0.4)	0	63	−16.6	−25.4	97
Br, +26.6	Na (0.4)	0	58	−15.7	−25.6	98
Br, +26.6	Na (0.1)	0	68	−16.0	−26.1	100

Table VI. Effect of *tert*-Butylamine (TBA) on the Reaction of (+)-(*S*)-2-Octyl Bromide and Chloride with $(CH_3)_3SnNa$[a] in THF at 0 °C[b]

$$(CH_3)_3SnNa + R^*-X \xrightarrow[THF,\ 0\ ^\circ C]{TBA} (CH_3)_3SnR^*$$

R*–X,[b] $[\alpha]_D^{25}$ (deg)	% yield of R*–$SnMe_3$	$[\alpha]_D^{25}$, deg obsd	$[\alpha]_D^{25}$, deg corr	enantiomeric excess, %
Br, +26.6[c]	45	−15.5	−25.3	97
Br, +31.8[d]	52	−9.09	−12.4	48
Cl, +30.5[d]	50	−21.1	−24.6	94

[a] Prepared from $(CH_3)_6Sn_2$ and sodium. [b] Concentration of $(CH_3)_3SnNa$ and *tert*-butylamine was 0.4 and 1.2–1.8 *M*, respectively. [c] Inverse addition: i.e., a solution of R*–X in THF was added to a well-stirred solution of $(CH_3)_3SnNa$ and TBA in THF. [d] Direct addition: i.e., a solution of $(CH_3)_3SnNa$ in THF was added to a well-stirred solution of R*–X and TBA in THF.

metalate anions may be less reactive but more stereoselective in certain substitution processes than are the corresponding alkyl analogoues. To confirm this hypothesis, we examined the reaction of Ph_3SnLi with optically active 2-bromooctane. The results, summarized below, reveal that under comparable conditions, triphenylstannate is, in fact, a substantially more stereoselective reagent than trimethylstannate.

$$(+)\text{-}(S)\text{-}2\text{-}C_8H_{17}Br + Ph_3SnLi \xrightarrow[25\ ^\circ C,\ 63\%]{THF} (-)\text{-}(R)\text{-}2\text{-}C_8H_{17}SnPh_3$$

$[\alpha]^{25}_D$ −23.3°, 100% *inversion*

Trapping Experiments. Kuivila and co-workers[9] recently reported results which suggest that certain additives can function as an efficient free radical trap of alkyl radicals generated during the reaction of trimethyltin anion with various alkyl halides. If correct, their results suggest that the coupling product produced by the addition of a THF solution of $(CH_3)_3SnNa$ to a stirred solution of 2-bromooctane (i.e., inverse-addition conditions) arises in large part (>70%)[9] through an electron-transfer pathway involving kinetically free 2-octyl radicals.

By contrast, our studies reveal that under equivalent conditions, i.e., inverse addition, the reaction of $(CH_3)_3SnNa$ with optically active 2-bromooctane is highly stereoselective and can even be stereospecific. We conclude that the procedures employed by these investigators must be introducing a substantial perturbation on the mechanism of this reaction[10] and that, therefore, such results cannot be considered as a reliable indication of the true mechanism(s) that obtains in the *absence* of these additives.[11]

Discussion

A comparison of the reaction of $(CH_3)_3SnLi$, -Na, and -K with *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylate, chloride, and bromide[2] and optically active 2-octyl tosylate, chloride, and bromide is characterized by strong parallels. Thus, an equivalent dependence of stereoselectivity on leaving group is apparent in both instances. Temperature, too, has an inverse effect on stereoselectivity in both systems. Solvent, gegenion, and concentration also appear to have a similar influence in both systems; however, this appearance is misleading for we have argued[2] that these influences in the *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide system affect the cis:trans product ratio and, therefore, are a reflection of the bimolecular reaction of the 4-*tert*-butylcyclohexyl radical with associated species such as $[(CH_3)_3SnM]_n$ and/or $[(CH_3)_3SnM]_n^{+\cdot}$, whose structures are likely to be gegenion, solvent, and concentration dependent. Structural changes in these reactants could well lead to changes in steric effects which are reflected in the transition state of the carbon–tin bond-forming step and hence in the stereochemistry of the carbon–tin coupling product.[2] Steric effects of this nature would be expected to influence the distribution of geometric but not optical isomers, since they result in kinetic distinctions which cannot distinguish between optical isomers. Hence, any difference in stereoselectivities resulting from variations in temperature, gegenion, solvent, concentration, etc. in the 2-octyl system must be a reflection of the initial partitioning between odd- and even-electron processes rather than the steric effects associated with C–Sn bond-forming step.

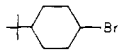
The reaction of *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide occurs with complete loss of stereochemical integrity while that of (+)-(*S*)-2-bromooctane takes place with a spectrum of stereoselectivities ranging from predominant, but by no means complete loss of stereochemistry, to stereospecific. This difference suggests that substitution in the acyclic system proceeds with more of an S_N2 component than it does in the cyclic system. Moreover, the present study sustains our earlier findings that a host of parameters including solvent, gegenion, nature of the leaving group

Table VII. A Comparison of the Normal- and Inverse-Addition Reaction of 2-Bromooctane and Sodium Trimethylstannate in THF at 0 °C in the Presence of *tert*-Butylamine and Dicyclohexylphosphine[a]

inverse addition					normal addition				
	% yield					% yield			
additive	octene	octane	2-octyltrimethyltin	Σ	additive	octene	octane	2-octyltrimethyltin	Σ
TBA,[c] 2.4 M	4.8	75	18	98	TBA,[f] 2.4 M	5.8	29	47	82
TBA,[d] 2.4 M	6.4	63	30	99	TBA,[g] 2.4 M	9.7	52	33	95
TBA,[c] 1.8 M	4.8	71	18	94					
DCPH,[d] 1.2 M	0.5	70	5	76	DCPH,[g] 1.2 M	0.6	60	4.8	65
DCPH,[e] 1.2 M	0.5	85	14	99	DCPH,[h] 1.2 M	0.5	63	6.5	70

[a] Concentration of TBA was 1.8–2.5 M and DCPH 1.2 M. [b] Yields were determined on a 24 ft × 1/8 in. HI-PAK column of SE-30 programmed from 50 to 200 °C at 6 °C/min. [c] Me_3SnNa was added using a slow-addition funnel. [d] Me_3SnNa was added slowly via syringe. [e] Me_3SnNa added rapidly via syringe. [f] 2-Bromooctane was added by using a slow-addition funnel. [g] 2-Bromooctane was added slowly by syringe. [h] 2-Bromooctane was added rapidly by syringe.

Table VIII. A Summary of the Stereochemical Consequences of the Reaction of Lithium Trimethylstannate, $(CH_3)_3SnLi$, with Various Alkyl Bromides in THF at 0 °C

R-Br	stereoselectivity, %	ref
$(CH_3)_3CHDCHDBr$	~80	24
$2\text{-}C_8H_{17}Br$	~30-100	this work
	~0	2

X, structure of the alkyl group R, temperature, and certain additives can affect the mechanisms by which alkylation of certain metalate ions occur. These results also illustrate the combined diagnostic utility of using geometrical and optical isomerism studies in tandem.

A comparison of the reaction of $(CH_3)_3SnM$ and Ph_3SnM with optically active 2-bromooctane is informative for it reveals that, although the former is a more reactive reagent than the latter, Ph_3SnM is nonetheless the more stereoselective reagent. Thus, the reaction with $(CH_3)_3SnM$ occurs readily at −20 °C while that with Ph_3SnM only displays a comparable reactivity when carried out at or near ambient temperature. Unlike $(CH_3)_3SnM$, however, the stereoselectivity of Ph_3SnM shows virtually no dependence on the order of reagent addition; indeed, the essentially stereospecific nature of its reaction with optically active 2-bromooctane seems largely unaffected by reaction parameters. The disparity between the stereoselectivity of $(CH_3)_3SnM$ and Ph_3SnM is substantially diminished, however, when the former alkylation reaction is carried out at −70 °C or under the conditions of inverse addition. It should be noted that any attempt to rationalize the differences in behavior between $(CH_3)_3SnM$ and Ph_3SnM must consider the important but as yet unknown (and quite possibly differing) aggregation of these reagents in solution. In the absence of this information, further discussion of these differences is unwarrented.

An examination of Tables I–III reveals that the partitioning between one- and two-electron process (free radical vs. S_N2 pathways) can be influenced by the method of preparation of the lithium, sodium, or potassium trimethylstannate. These observations are reasonable if it is assumed that the residual alkali halide affects principally the carbon–halogen bond rupture process (i.e., affects the partitioning between electron-transfer and S_N2 pathways).[12] In this regard it is noteworthy that the presence or absence of metal halides has been noted to effect substantial differences in the reactivities of a number of other organometallic reagents.[13] We have not investigated this phenomenon in the present instance in further detail.

Two additional findings are revealed by the present study. First, the order of reagent addition has a dramatic influence on reaction stereoselectivity. The reason(s) for this behavior is (are not obvious; however, one possibility is that such behavior is a reflection of the influence which the degree of association of $(CH_3)_3SnM$ and/or ion pairing has on the partitioning between odd- and even-electron processes.[26] Further discussion of these findings must await more detailed information concerning the nature of these reagents in solution. Second, certain additives (for example, alkali halides, *tert*-butylamine, and dicyclohexylphosphine) can alter the mechanism of the reaction of $(CH_3)_3SnM$ with alkyl halides.

A summary of the partitioning between one- and two-electron substitution pathways observed during the alkylation of lithium trimethylstannate with various alkyl bromides is presented in Table VIII. Collectively, these results illustrate the range of mechanistic situations that result during the alkylation of lithium trimethylstannate by selected primary and secondary alkyl bromides.

Finally, the preparation of the optically pure compounds **1** and **2** merits brief discussion in its own right. Previous preparations of R*–SnR'_3 by direct alkylation procedures relied on a modification of the correlations of Brewster[14] (the bond refraction-molecular rotation correlation) for sterochemical assignment,[27] while relying on accumulated stereoselectivity and the assumption that the bromine cleavage of R*–SnR'_3 was stereospecific in order to determine the absolute rotations of these compounds.[15] The synthesis of optically pure **1** and **2** reported here does not suffer these disadvantages. Their ready availability will facillitate a wide variety of mechanistic studies including those of free radical (S_H2) substitutions as well as electrophilic processes. Moreover, several advantages accrue from the choice of the 2-octyl group as a chiral probe. In particular, the 2-octyl group virtue of its molecular weight, allows for the greater ease of isolation and handling of those derivatives anticipated as C–Sn cleavage products in subsequent studies.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under an atmosphere of prepurified nitrogen. Tetrahydrofurn (THF) and diethyl ether were distilled under nitrogen from lithium aluminum hydride immediately before use. Dimethoxyethane (DME) was distilled from sodium/benzophenone ketyl. Optically active 2-octanol (Aldrich Chemical Co.), trimethyltin chloride (ROC/RIC), triphenyltin chloride (from M + T Chemicals), hexamethylditin (Orgmet, Inc.), trimethyltin bromide (Orgmet, Inc.), dicyclohexylphosphine (Aldrich Chemical Co.), *tert*-butylamine (Aldrich Chemical Co.), and copper iodide (Fisher Scientific Co.) were all used without further purification. Methyllithium in diethyl ether was purchased from Lithium Corp. of America and standardized by the Gilman double-titration method. Lithium metal (200μ dispersion, 50% by weight in mineral oil) was purchased from Lithium Corp. of America.

Melting points and boiling points are uncorrected. Infrared spectra were taken in sodium chloride cells on a Perkin-Elmer 727B grating spectrometer. ^1H NMR spectra were recorded on a Varian T-60 spectrometer; chemical shifts are reported in parts per million downfield from $(CH_3)_4Si$. Optical rotations were obtained as neat liquids in a 0.1-dm cell or as benzene solutions in a 1-dm cell employing a Perkin-Elmer Model 141 spectropolarimeter using 589-nm radiation.

Analytical GLPC analyses were performed on a Varian 90-P instrument with a Hewlett-Packard 3380A integrator using internal standard techniques with response factors obtained by using authentic samples. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS. HPLC separations were performed on a Waters Associates Model 6000A system. A Vacuum Atmosphere glovebox was used to transfer all air- and moisture-sensitive solids.

(+)-(*S*)-2-Octyl bromide was prepared from (-)-*R*-2-octanol by either of two literature procedures[17,20] and had bp 71 °C (12 torr) [lit.[20] bp 72 °C (9 torr)].

(-)-(*R*)-2-Octyl tosylate was prepared from (-)-(*R*)-2-octanol as described by Streitwieser.[22]

***cis*- and *trans*-4-*tert*-Butylcyclohexyl bromides** were prepared as described previously.[2]

(13) Cf. Casey, C. P. Ph.D. Thesis, MIT, Cambridge, MA, 1969. Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York , 1968. Stedronsky, E. R. Ph.D. Thesis, MIT, Cambridge, MA, 1970.

(14) Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5475.

(15) Davis, D. D.; Jensen, F. R. *J. Org. Chem.* **1970**, *35*, 3410.

(16) There are several inconsistencies in the literature with respect to the currently accepted values for the rotation of optically pure (neat) 2-chloro- and 2-bromooctane. Some of these reports are premised on a value for the rotation of optically pure (neat) 2-octanol of $[\alpha]^{20}_D$ +8.02°.[17] An earlier[18] as well as a more recent[19] determination of this value suggest that a more accurate value is $[\alpha]^{17}_D$ +9.90°. It is this latter value that we have employed in all our calculations.

Three independent investigators have reported the following values for the rotation of purportedly optically pure (-)-2-chlorooctane: $[\alpha]^{20}_D$ −31.6°,[17] $[\alpha]^{20}_D$ −32.4°,[19] and $[\alpha]^{22}_D$ −36.15°. In our hands preparation of this material by an alternative procedure[20] yields (-)-2-chlorooctane with a rotation of $[\alpha]^{20}_D$ −37.3°; it is this last value which we have used in calculating the data in Tables I–VI.

Several values have been reported for the rotation of purportedly optically pure (-)-2-bromooctane: $[\alpha]^{20}_D$ −40.6°,[18] $[\alpha]^{20}_D$ −44.3°,[19]. Preparation of this material in our hands yielded (-)-2-bromooctane with $[\alpha]^{20}_D$ −43.4°. In carrying out the calculations presented in Tables I–VI, we have employed this last value for the rotation of optically pure (-)-2-bromooctane.

(17) Hudson, H. R. *Synthesis* **1969**, *1*, 112.

(18) Brauns, H. *Recl. Trav. Chim. Pays-Bas* **1946**, *65*, 799.

(19) Hoffman, H. M. R. *J. Chem. Soc.* **1964**, 1249.

(20) San Filippo, J., Jr.; Romano, L. J. *J. Org. Chem.* **1975**, *40*, 1514.

(21) Coulson, E. J.; Gerrard, W.; Hudson, H. R. *J. Chem. Soc.* **1965**, 2364.

(22) Streitwieser, A., Jr.; Walsh, T. D.; Wolfe, J. R., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3682.

(+)-(S)-2-Octyl chloride was prepared from (-)-(R)-2-octanol as previously described:[20] bp 69.5–71.0 °C (20 torr) [lit.[20] 61–62 °C (17 torr)].

Cyclopropylcarbinyl bromide, prepared as described by Meek and Rowe,[23] had bp 52.5–53.5 °C (91 torr) [lit.[23] 101.5–102.5 °C (627 torr)].

Normal-Addition Reaction of (+)-(S)-2-Octyl Bromide and Lithium Trimethylstannate (Prepared from Trimethyltin Chloride and Lithium) (Typical Procedure). Following several rinses with dry pentane in a glovebox to remove its mineral oil coating, lithium (0.140 g as Li, 20.2 mmol) was placed in a flame-dried, 40-mL centrifuge tube with a Teflon-coated magnetic stirrer bar. The vessel was capped with a rubber septum and placed in a water bath (25 °C). A solution of trimethyltin chloride (0.796 g, 4.00 mmol) in THF (10 mL) was added through a stainless steel cannula. The resulting green solution was allowed to stir for 15 min and then filtered through a 145–175-μm fritted-glass filter into a 25-mL, two-necked, flame-dried flask chilled to 0 °C and equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow addition funnel stoppered with a rubber septum and containing a solution of (+)-(S)-2-octyl bromide ($[\alpha]^{25}_D$ +39.6° (optical purity 91%; 0.733 g, 4.00 mmol) in THF (8 mL) along with 2-methyltridecane (0.194 g) as internal standard. Addition was carried out over a 0.5-h period. The resulting reaction mixture was quenched immediately with water (10 mL) and extracted with petroleum ether. The organic layer was dried ($MgSO_4$), filtered and concentrated. The yield of (-)-(R)-2-octyltrimethyltin ($[\alpha]^{25}_D$ -12.6°, neat) was 69% as determined by GLPC on a 6 ft × 0.125 in. column of UCW-98 at 130 °C: mass spectrum, *m/e* 263 (2.5), 169 (17), 167 (14), 165 (100), 164 (30), 163 (77), 162 (27), 161 (48), 157 (3.5), 155 (6), 153 (6), 151 (38), 150 (20), 149 (32), 148 (16), 147 (20).

Reaction of (+)-(S)-2-Octyl Bromide and Lithium Triphenylstannate (Prepared from Triphenyltin Chloride and Lithium) (Typical Procedure). After several rinses with dry pentane in a glovebox to remove the mineral oil coating, lithium (0.140 g, 20.2 mmol) was placed in a flame-dried, 40-mL centrifuge tube containing a Teflon-coated magnetic stirrer bar and capped with a rubber septum. The centrifuge tube was placed in a water bath (25 °C), and a solution of triphenyltin chloride (1.54 g, 4.00 mmol) in THF (10 mL) was added through a cannula. The resulting green solution was allowed to stir for 1 h and then filtered through a 145–175-μm fritted-glass filter into a 25-mL, two-necked, flame-dried flask containing a Teflon-coated magnetic stirrer bar and equipped with a 30-mL Kontes slow addition funnel stoppered with a rubber septum containing a solution of (+)-(S)-2-octyl bromide ($[\alpha]^{25}_D$ +38.60° (optical purity 89%; 0.733 g, 4.00 mmol) in THF (8 mL) along with dodecane (0.194 g) as internal standard. Addition was completed after 0.5 h and the resulting reaction mixture allowed to stir at 25 °C for an additional hour before adding water (10 mL). The organic layer was dried ($MgSO_4$) and concentrated. Analysis by HPLC (μ-Bondapak-C_{18}, acetonitrile liquid phase) indicated a 63% yield of (-)-(R)-2-octyltriphenyltin ($[\alpha]^{23}_D$ -20.6° (*c* 4.14, benzene)): ^1H NMR (CCl_4) δ 0.65–2.6 (17 H, m), 7.0–8.3 (15 H, m, C_6H_5); mass spectrum, *m/e* (0.3), 464 (0.2), 353 (16), 352 (21), 351 (100), 350 (41), 349 (80), 348 (31), 347 (43).

Inverse-Addition Reaction of (+)-(S)-2-Octyl Bromide and Sodium Trimethylstannate (Prepared from Sodium and Hexamethylditin) (Typical Procedure). Sodium (50% dispersion in paraffin, 0.20 g, 8.7 mmol) was placed in a flame-dried, 40-mL centrifuge tube equipped with a Teflon-coated magnetic stirrer bar and quickly capped with a rubber septum. The dispersion was washed three times with dry pentane to remove excess paraffin. Dry THF (10 mL) was added by syringe followed by the addition of hexamethylditin (0.684 g, 2.08 mmol), and the mixture was allowed to stir for 1 h at room temperature. The resulting mixture was centrifuged and the supernatant solution transferred via cannula through a 145–175-μm fritted-glass filter into a 30-mL Kontes slow-addition funnel. This solution was then added to a cooled (0 °C) solution of (+)-(S)-octyl bromide ($[\alpha]^{25}_D$ +26.6°, optical purity 61%; 0.775 g, 4.00 mmol) in THF (8 mL) over a period of 0.25 h. The resulting reaction was stirred for an additional 2 h at 0 °C and then quenched with water (10 mL). The organic layer was dried ($MgSO_4$) and concentrated. The yield of (-)-(R)-2-octyltrimethyltin ($[\alpha]^{25}_D$ -15.7° (neat)) was 40% as determined by GLPC on a 6-ft × 0.125-in. column of UCW-98 at 138 °C.

Reaction of (+)-(S)-2-Octyl Bromide and "$[(CH_3)_3Sn]_2CuLi$" (Typical Procedure). Following several rinses with dry pentane in a glovebox to remove its mineral oil coating, lithium (50% dispersion, 200 μm; 0.21 g as Li, 30 mmol) was placed in a flame-dried, 40-mL centrifuge tube equipped with a Teflon-coated magnetic stirrer bar, and the tube capped with a rubber septum. The centrifuge tube was placed in a water bath (25 °C), and a solution of trimethyltin chloride (1.88 g, 5.97 mmol) in 6 mL of THF was added via cannula with rapid stirring. The resulting green solution was allowed to stir for 15 min, then cooled to -78 °C, and filtered through a 145–175-μm fritted-glass filter into a 50-mL, three-necked, flame-dried flask containing 0.668 g (3.51 mmol) of copper iodide suspended in 3 mL of THF at -78 °C and equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow-addition funnel stoppered with a rubber septum and which contained a solution of 0.193 g (1.00 mmol) of (+)-(S)-2-octyl bromide ($[\alpha]^{25}_D$ + 34.9°, optical purity 80%) and 0.127 g of 2-methyltridecane internal standard) in 2 mL of THF. Addition was carried out over a 0.25-h period with rapid stirring; the resulting solution was stirred for an additional 2 h at -78 °C and then allowed to slowly warm to room temperature. This mixture was then treated with 1 mL of water, filtered through a short column of alumina and dried ($MgSO_4$). The yield of (R)-2-octyltrimethyltin ($[\alpha]^{25}_D$ -20.9° (neat)) was 81% as determined by GLPC on a 6-ft × 0.125-in. column of UCW-98 at 130 °C.

Normal-Addition Reaction of (+)-(S)-2-Octyl Bromide and Lithium Trimethylstannate (Prepared from Hexamethylditin and Methyllithium) (Typical Procedure). Methyllithium (4.0 mmol in 2.7 mL of ether) was added to 1.33 g (4.06 mmol) of hexamethyliditin in 12 mL of THF in a 25-mL, two-necked, round-bottomed flask equipped with a 30-mL slow-addition funnel and a Teflon-coated magnetic stirrer bar. The solution was allowed to stir at room temperature for 30 min and then cooled to 0 °C. (+)-(S)-2-Octyl bromide ($[\alpha]^{23}_D$ +38.1°, 87% optical purity; 0.761 g, 3.94 mmol) in THF (8 mL) was added over a 20-min period. The resulting mixture was allowed to stir at 0 °C for an additional hour and then poured into 15 mL of aqueous NH_4Cl, and the organic layer was separated, dried ($MgSO_4$) and concentrated. The yield of (-)-(R)-2-octyltrimethyltin ($[\alpha]^{23}_D$ -11.4° (neat, 44% optical purity) was 75% as determined by GLPC analysis on a 6-ft × 0.125-in. column of UCW-98 at 130 °C.

Normal-Addition Reaction of (+)-(S)-2-Octyl Bromide and Sodium Trimethylstannate (Prepared from Hexamethylditin and Sodium) (Typical Procedure). Sodium (50% dispersion in paraffin, 0.20 g, 8.7 mmol) was placed in a flame-dried, 40-mL centrifuge tube equipped with a Teflon-coated magnetic stirrer bar and quickly capped with a rubber septum. The dispersion was washed three times with dry pentane to remove excess paraffin. Dry THF (10 mL) was added by syringe followed by the addition of hexamethylditin (0.6803 g, 2.09 mmol), and the mixture was allowed to stir for 1 h at room temperature. The resulting mixture was centrifuged and the supernatant transferred via cannula through a 70–100-μm fritted-glass filter into a 25-mL, two-necked, flame-dried flask cooled to 0 °C and equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow-addition funnel stoppered with a rubber septum and containing a solution of (+)-(S)-2-octyl bromide ($[\alpha]^{26}_D$ + 33.2°, optical purity 76%; 0.771 g, 3.99 mmol) in THF (8 mL) along with 2-methyltridecane (0.202 g) as internal standard. The addition was carried out over 0.5 h. The resulting reaction mixture was then quenched with water (10 mL) and extracted with petroleum ether. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The yield (-)-(R)-2-octyltrimethyltin ($[\alpha]^{25}_D$ -8.73°, neat) was 77% as determined by GLPC on a 6-ft × 0.125-in. column of UCW-98 at 130 °C.

Control Experiments. In separate experiments, authentic *cis*- and *trans*-(4-*tert*-butylcyclohexyl)trimethyltin were allowed to stir with halide-containing $(CH_3)_3SnLi$ in THF under typical reaction conditions. Workup followed by GLPC analysis revealed no observable (<1%) isomerization of either isomer.

In a related experiment, an excess of optically active 2-bromooctane was added slowly to a stirred solution of $(CH_3)_3SnLi$ in THF at 0 °C. Following workup, the unreacted halide was recovered. Its optical rotation indicated no isomerization had occurred.

Registry No. (R)-**1**, 79055-01-9; (S)-**1**, 79054-99-2; **2**, 79055-00-8; *cis*-**3**, 5009-36-9; *trans*-**3**, 5009-37-0; *cis*-**4**, 38630-14-7; *trans*-4, 64871-28-9; $(CH_3)_3SnLi$, 17946-71-3; $(CH_3)_3SnNa$, 16643-09-7; $(CH_3)_3SnK$, 56859-17-7; $(CH_3)_3SnCl$, 75-77-4; (S)-2-octyl bromide, 1191-24-8; (S)-2-octyl chloride, 1191-24-8; (R)-2-octyl tosylate, 27770-99-6; (R)-2-octanol, 5978-70-1; cyclopropylcarbinyl bromide, 7051-34-5; (cyclopropylcarbinyl)trimethyltin, 51675-53-7; 3-butenyltrimethyltin, 17314-38-4; octane, 111-65-9; octene, 25377-83-7; Ph_3SnLi, 791-30-0.

(23) Meek, J. S.; Rowe, J. W. *J. Am. Chem. Soc.* **1955**, *77*, 6675.
(24) Bock, P. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2826.
(25) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.
(26) Cf. Zieger, H.; Mathisen, D. *J. Am. Chem. Soc.* **1979**, *101*, 2207.
(27) The validity of this procedure is questionable: Lee, K.; San Filippo, J., Jr., manuscript in preparation.