cm) established the compound to be 98% ee.

Allylboration of the Higher Aldehydes. The procedure, essentially as described above, was applied to the other representative aldehydes (Table I). All of the products are known, and the individual isolation procedures have been fully described in our previous publications.[6]

Acknowledgment. The financial support of the National Institutes of Health (Grant GM 10937) and Dow Chemical Co. is gratefully acknowledged. We also thank Dr. Suk Dev (Malti Chem Labs, Baroda, India) for providing us with a generous gift of (+)-2-carene.[4]

Registry No. 1, 124821-92-7; **5**, 4497-92-1; **6**, 114533-27-6; **7**, 124821-93-8; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; *n*-butyraldehyde, 123-72-8; 2-methylpropionaldehyde, 78-84-2; 2,2-dimethylpropionaldehyde, 630-19-3; acrolein, 107-02-8; benzaldehyde, 100-52-7; (*S*)-4-penten-2-ol, 555563-79-6; (*S*)-5-hexen-3-ol, 62959-96-0; (*S*)-1-hepten-4-ol, 85520-72-5; (*R*)-2-methyl-5-hexen-3-ol, 88691-75-2; (*R*)-2,2-dimethyl-5-hexen-3-ol, 88691-76-3; (*R*)-1,5-hexadien-3-ol, 119596-43-9; (*R*)-1-phenyl-3-buten-1-ol, 85551-57-1.

Synthetic Utility and Mechanistic Studies of the Aliphatic Reverse Brook Rearrangement

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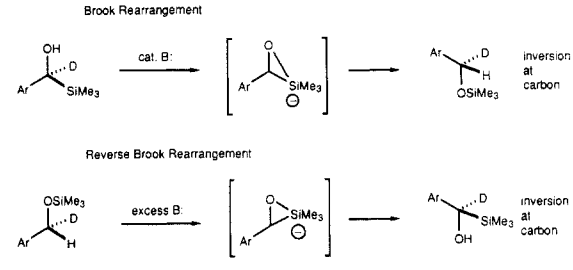
Abstract: The aliphatic reverse Brook rearrangement has been examined in detail. Transmetalation of [α-[(trialkylsilyl)oxy]alkyl]trialkylstannanes occurs via a complex equilibrium favoring the most stable carbanion. The aliphatic reverse Brook rearrangement is driven forward by the rapid migration of silicon from O to C in a transient α-silyloxy carbanion due to the formation of the more stable lithium alkoxide. Cross-over experiments have shown that the rearrangement is an intramolecular process while incorporation of a radical trap revealed that the rearrangement does not involve radical intermediates. Studies of configurationally fixed stannanes derived from 4-*tert*-butylcyclohexanone concluded that the rearrangement occurs with retention of configuration. Preparation and reverse Brook rearrangement of optically active (*S*)-[α-[(trimethylsilyl)oxy]-hexyl]tributylstannane (98% ee) provided 1-(trimethylsilyl)hexanol in 97% ee. The synthetic utility of this method for the preparation of a variety of (α-hydroxyalkyl)trialkylsilanes from aldehydes has also been demonstrated.

The Brook rearrangement[1] is a stereospecific intramolecular migration of silicon from carbon to oxygen which occurs for (α-hydroxybenzyl)trialkylsilanes in the presence of a catalytic amount of base. The rearrangement is driven forward by the increased thermodynamic stability of the silyl ether product relative to the alcohol starting material due to the formation of a Si–O bond in place of a Si–C bond. Brook and co-workers[1b] established that the rearrangement proceeds with inversion of configuration at carbon and retention of configuration at silicon. The reverse or anti-Brook rearrangement,[2] the migration of silicon from oxygen to carbon, has been accomplished by deprotonation of α-(trialkylsilyl)oxy benzyl ethers. Wright and West[2a] studied the reverse rearrangement of (aryloxy)silyl ethers in detail, observing that the reaction is similar to the forward Brook rearrangement in that the migration of silicon is intramolecular and stereospecific. Deprotonation of a homochiral benzyloxy silyl ether and subsequent rearrangement resulted in the homochiral (α-hydroxybenzyl)silane of inverted configuration at carbon. The reverse Brook rearrangement requires excess base and is driven forward due to the stability of the alkoxide anion product relative to the carbanion starting material. These studies are summarized in Scheme I.

More recent studies by Ireland et al.[3a] and Danheiser and co-workers[3b] have illustrated that the reverse Brook rearrangement also occurs for allylic silyl ethers upon deprotonation with strong base. Cohen and Matz[4] had also observed a reverse Brook rearrangement of an allyl anion generated by the reductive lithiation of an allylic phenylthio ether. In all of the above examples, a single regioisomer of the α-hydroxyallyl silane product is produced. We reasoned that the same process should occur for aliphatic systems, in analogy with the Wittig rearrangement,[5] if the requisite carbanion could be easily generated. By incorporating a transmetalation (Sn to Li) as part of the process, we were able to successfully carry out the aliphatic reverse Brook rearrangement via the intermediacy of an [α-[(trialkylsilyl)oxy]alkyl]trialkylstannane.[6] In this paper, we present a full account of this method

Scheme I. Summary of the Brook and Reverse Brook Rearrangement on Aryl-Substituted Species



(1) (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77–84. (b) Brook, A. G.; Pascoe, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 6224–6227. (c) Brook, A. G.; Bassendale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, pp 149–227.

(2) (a) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214–3222. (b) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3227–3232.

(3) (a) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668–3670. (b) Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y. M.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393–5396. (c) Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y. M.; Szczepanski, S. W. *Org. Synth.* **1987**, *66*, 14–21. (d) Scheller, M. E.; Frei, B. *Helv. Chim. Acta* **1985**, *68*, 44–52.

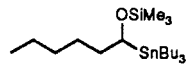
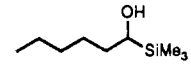
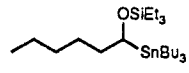
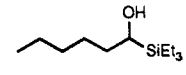
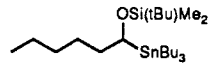
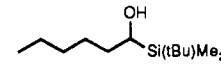
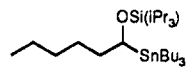
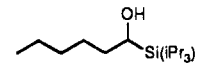
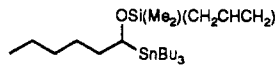
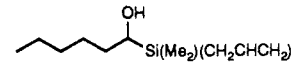
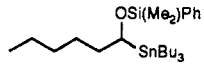
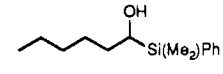
(4) Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900–6902.

(5) (a) Schollkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 763. (b) Garst, J. F.; Smith, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 1526–1537. (c) Lee, B. H.; Biswas, A.; Miller, M. J. *J. Org. Chem.* **1986**, *51*, 106–109. (d) Schreiber, S. L.; Goulet, M. T. *Tetrahedron Lett.* **1987**, *28*, 1043–1046. (e) Eisch, J. J.; Galle, J. W.; Piotrowski, A.; Tsai, M.-R. *J. Org. Chem.* **1982**, *47*, 5051–5056.

(6) Preliminary reports of this chemistry have appeared: (a) Linderman, R. J.; Ghannam, A. *J. Org. Chem.* **1988**, *53*, 2878–2880. (b) Ghannam, A.; Linderman, R. J. *Abstract of Papers*, 197th National Meeting American Chemical Society, Dallas, TX, April 9–14, 1989; American Chemical Society: Washington, DC, 1989; ORGN-197.

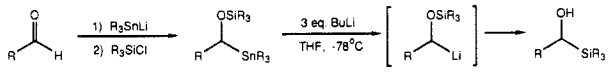
0002-7863/90/1512-2392$02.50/0

Table I. Synthesis of (α-Hydroxyalkyl)trialkylsilanes via a Reverse Brook Rearrangement Steric Limitations at Silicon

entry	stannane	method of silylation[a]	silane	yield, %[b]
1	 **1**	A	 **2**	56
2	 **3**	B	 **4**	54
3	 **5**	B	 **6**	68
4	 **7**	B	 **8**	40
5	 **9**	C	 **10**	61
6	 **11**	D	 **12**	60

[a] O-Silylation was accomplished by one of four methods described in the Experimental Section: A, with TMSCN; B, with R_3SiOTf, C, with R_3SiCl and a crown ether; D, with R_3SiCl and Hunigs base. [b] Overall isolated yield from hexanal.

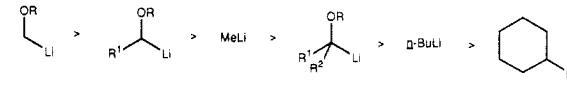
illustrating the synthetic utility of the procedure as a method for the direct synthesis of (α-hydroxyalkyl)trialkylsilanes and detailing the mechanistic and stereochemical features of the reaction.



Synthesis of (α-Hydroxyalkyl)trialkylsilanes. The direct synthesis of (α-hydroxyalkyl)trialkylsilanes by nucleophilic addition of a trialkylsilyl metallo anion to an aldehyde or ketone is not readily accomplished. Although there are some reports of the condensation reaction of (trimethylsilyl)lithium with ketones,[7] and to non-enolyzable aldehydes,[8] the generality of this direct approach is limited and has been viewed as not being synthetically useful.[8b] Replacement of one of the alkyl groups on silicon with an aryl substituent does provide a silyl anion that can undergo condensation reactions in reasonable yields.[9] The tin-mediated reverse Brook rearrangement alleviates the problem of generating the trialkylsilyl anion and allows silicon to be introduced as an electrophile.

Trialkylstannyl anions[10,11] add to aldehydes quite efficiently, providing an alkoxide intermediate that can be O-silylated by one of several methods. Trialkylsilyl chlorides are inefficient silylating agents while the corresponding trialkylsilyl cyanide or triflate works well. As an alternative, trialkylsilyl chlorides can be employed if a catalytic amount of benzo-15-crown-5 is added to the reaction mixture. Phenyldimethylsilyl chloride can serve as the electrophile if an excess of Hunigs base (*N*,*N*-diethylisopropylamine) and catalytic 4-(*N*,*N*-dimethylamino)pyridine are combined with the (α-hydroxyalkyl)tributylstannane obtained by aqueous workup of the initial condensation reaction. The [α-[(trialkylsilyl)oxy]alkyl]trialkylstannane is then treated with 3 equiv of *n*-butyllithium (BuLi) in tetrahydrofuran (THF) at −78 °C to affect transmetalation and rearrangement. Therefore, a variety of alkyl-substituted (α-hydroxyalkyl)trialkylsilanes can be prepared by this method (Table I). Even the very sterically encumbered triisopropylsilyl moiety can be employed (Table I, entry 4); however, the rearrangement does not go to completion. In this example, 10–15% of the intermediate stannane **7** can be recovered from the reaction mixture. A phenyl-substituted silyl ether (Table I, entry 6) also undergoes the rearrangement in a reasonable overall yield from hexanal. In all of the cases examined, the transmetalation/rearrangement step proceeded in good to excellent yield (60–98%), while the initial condensation and O-silylation step was less efficient (60–65%).

Scheme II. Relative Stabilities of (α-Alkoxyalkyl)- and Alkyllithium Reagents (from Ref 12c)

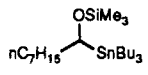
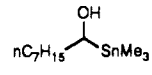
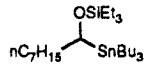
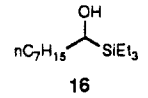
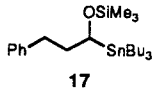
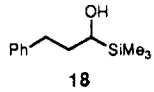
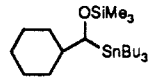
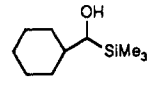
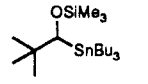
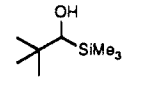
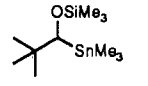
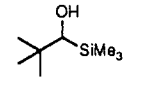
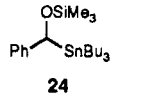
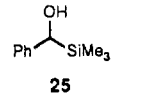
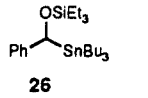
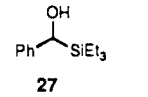
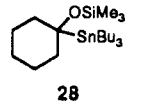
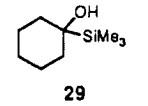
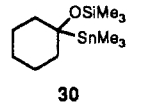
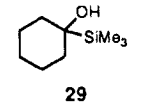
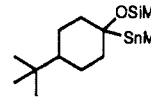
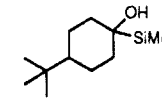


The transmetalation and rearrangement of α-[(trialkylsilyl)-oxy]alkyl]stannanes is a general reaction. Several examples are presented in Table II, illustrating the tolerance for alkyl substitution adjacent to the ether substituent. For highly hindered alkyl substrates, such as the *tert*-butyl-substituted stannane **21**, rearrangement did not occur via the standard procedure described above. However, substituting (trimethylstannyl)lithium[11] for (tributylstannyl)lithium in the initial condensation step provides the trimethylstannyl derivative **23**, which does undergo the rearrangement.

In attempts to extend the reaction to ketones, only α-(trimethylsilyl)oxy-substituted stannanes could be generated. All attempts at O-silylation with triethylsilyl triflate failed, leading only to polymerization of the solvent (THF) and formation of $Me_3SnSiEt_3$. The tin–silicon product arises by a reversal of the initial condensation product, regenerating the ketone and (trimethylstannyl)lithium. The reversal of the trialkylstannyl anion

(7) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063–3064.
(8) (a) Corey, E. J.; Tius, M. A.; Das, J. *J. Am. Chem. Soc.* **1980**, *102*, 1742–1744. (b) Wilson, S. R.; Hague, M. S.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 747–748. (c) Vedejs, E.; Arnest, M. J.; Eustache, J. M.; Krafft, G. A. *J. Org. Chem.* **1982**, *47*, 4384–4386.
(9) (a) Reich, H. J.; Eisenhart, E. K. *J. Org. Chem.* **1984**, *49*, 5282–5283. (b) Reich, H. J.; Eisenhart, E. K.; Olson, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 7791–7800. (c) Reich, H. J.; Holtan, R. C.; Borkowsky, S. L. *J. Org. Chem.* **1987**, *52*, 312–314. (d) Cuadrado, P.; Gonzalez, A. M.; Gonzalez, B.; Pulido, F. J. *Synth. Commun.* **1989**, *19*, 275–283.
(10) (Tributylstannyl)lithium may be prepared from hexabutylditin or from tributyltin hydride (ref 12a). The α-silyloxy stannanes prepared in this study employed (tributylstannyl)lithium generated from tributyltin hydride via deprotonation with lithium diisopropylamide.
(11) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836–4838.

Table II. Synthesis of (α-Hydroxyalkyl)trialkylsilanes via a Reverse Brook Rearrangement Steric and Electronic Factors at Carbon

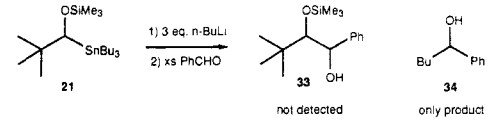
entry	stannane[a]	silane[b]	yield, %[c]
1	 **13**	 **14**	67
2	 **15**	 **16**	63
3	 **17**	 **18**	56
4	 **19**	 **20**	57
5	 **21**	 **22**	0[d]
6	 **23**	 **22**	49[e]
7	 **24**	 **25**	65
8	 **26**	 **27**	60
9	 **28**	 **29**	0[f]
10	 **30**	 **29**	50
11	 **31**	 **32**	40[g]

[a] Obtained via trialkyltin anion addition to the appropriate carbonyl precursor. [b] Obtained by the standard rearrangement conditions described in the Experimental Section (3 equiv of BuLi). [c] Overall yield of isolated product from the carbonyl precursor. [d] Stannane **21** recovered in >90% yield. [e] Yield of **22** reduced due to the volatility of the product. [f] Stannane **28** recovered in >95% yield. [g] See text for stereochemical assignment.

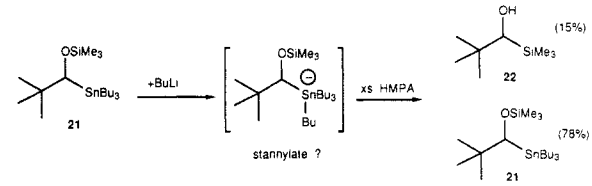
carbonyl condensation reaction typically does not occur at low temperatures;[12] however, this process is rapid at 0 °C.[13] Matteson and co-workers[14] have also recently observed decomposition of similar intermediates produced from sterically demanding substrates.

Mechanistic Studies: Transmetalation and Rearrangement. In our preliminary studies,[6] we determined that an excess of BuLi was required for the transmetalation/rearrangement reaction using either the tributyl- or trimethylstannyl precursor. In general, Sn to Li transmetalation reactions of α-alkoxyorganostannanes are very efficient, requiring only a slight excess of BuLi.[12,13] To probe the unusual stoichiometry required for the reverse Brook rearrangement, we chose to examine the reaction of stannanes **21** and **23** with BuLi in more detail.

Preliminary studies indicated that **21** would not undergo transmetalation/rearrangement in THF or dimethoxyethane using the standard reaction conditions of 3 equiv of BuLi at −78 °C for 15 min. An alternative reaction pathway involving nucleophilic attack at the silicon atom of the silyl ether moiety was ruled out by the recovery of starting material **21** with an excellent material balance (>95%). The generation of a stable anionic intermediate was tested by two separate trapping experiments. Attempts to incorporate deuterium by quenching the reaction mixture with deuterium oxide and analysis of recovered **21** by high-resolution mass spectrometry ruled out an anomalous deprotonation reaction. Treatment of the transmetalation reaction mixture with an excess of benzaldehyde led only to **34** in 63% isolated yield with no trace of the possible α-silyloxy anion adduct **33**.[15]



The possibility of formation of a stable stannylate intermediate[16] was also investigated. ^{119}Sn NMR analysis of a mixture of **21** and BuLi in THF at −78 to 0 °C revealed only the stannane **21** at −28 ppm (relative to Bu_4Sn) with no other observable signals. Reich and Phillips[17] have observed stannylate anions in THF in the presence of HMPA, but not in THF alone. Upon addition of HMPA to the NMR tube containing **21** and BuLi, transmetalation did occur as evidenced by formation of Bu_4Sn. In all attempts to discern a stannylate intermediate, no ^{119}Sn NMR signals other than **21** and Bu_4Sn were observed. One must note that this negative evidence does not rule out formation of a short-lived stannylate intermediate that would not be observed on the NMR time scale. On a preparative scale, the rearrangement of **21** to **22** using 1 equiv of BuLi was possible if 3 equiv of HMPA were added to the reaction mixture. However, **21** could not be completely consumed even after prolonged reaction times (>4 h) and the yield (15%) of **22** was substantially lower than that obtained by transmetalation/rearrangement of **23**.



(12) (a) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481–1487. (b) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201–1202. (c) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842–853. (d) Duchene, A.; Quintard, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 29–30. (e) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1984**, 800–802. (f) Lesimple, P.; Beau, J.-M.; Sinay, P. *J. Chem. Soc., Chem. Commun.* **1985**, 894–895. Additional examples of the preparation and synthetic applications of α-alkoxyorganostannanes can be obtained from references within 12a–f; see also refs 13, 14, and 29.

(13) Linderman, R. J.; Godfrey, A.; Horne, K. *Tetrahedron* **1989**, *45*, 495–506.

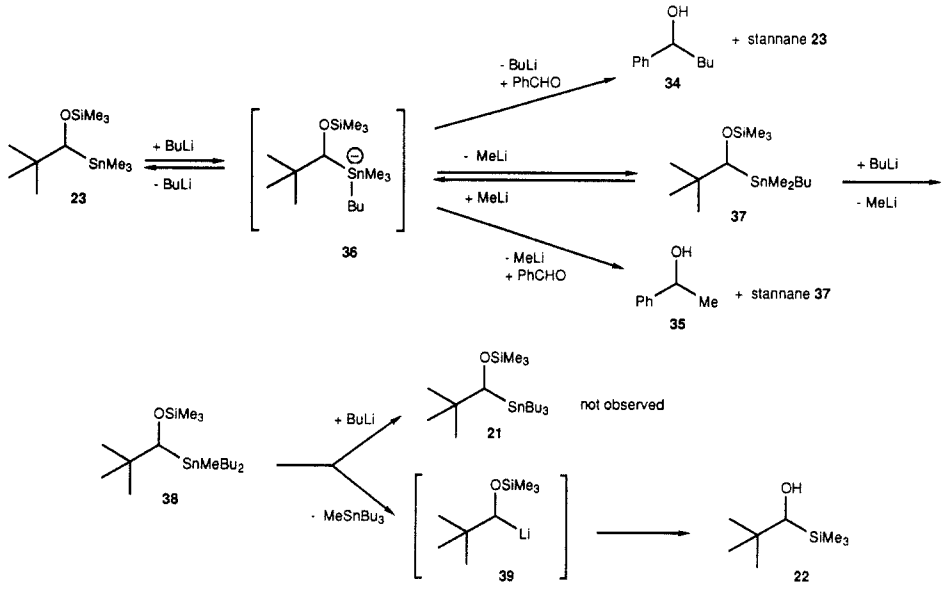
(14) Matteson, D. S.; Tripathy, P. B.; Sarkar, A.; Sadhu, K. M. *J. Am. Chem. Soc.* **1989**, *111*, 4399–4402.

(15) The diol was prepared independently by condensation of the lithio anion generated from 2,2-dimethyl-1-(methoxymethoxy)-1-(tri-*n*-butylstannyl)propane[13] and benzaldehyde, followed by hydrolysis of the acetal protecting group.

(16) Still[12a] had ruled out the possibility of a stannylate intermediate in the transmetalation of an (α-methoxyalkyl)tributylstannane by a competition experiment. McGarvey and co-workers[12c] observed Sn–Li exchange processes by low-temperature ^{1}H NMR and failed to observe any intermediate stannylate complexes. Both of these studies concluded that an equilibrium of alkyllithium and (α-alkoxyalkyl)lithium species was established that favored the more stable anionic species. Reich and Phillips,[17] however, have demonstrated that stannylate intermediates can be prepared and observed on the NMR time scale dependent upon the reaction conditions.

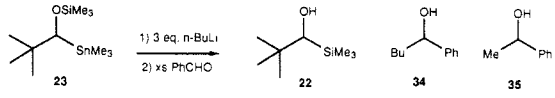
(17) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102–2103.

Scheme III. Potential Route for Me–Bu Conversion and Rearrangement of Stannane **23**



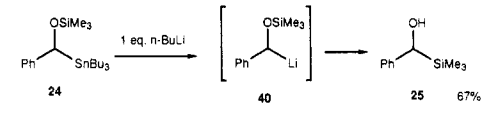
McGarvey and co-workers[12c] have determined the relative stability of α-alkoxyorganolithio anions compared to alkyllithium species as that shown in Scheme II. In the examples shown, the alcohol protecting group (an acetal) may provide additional stabilization of the lithio anion via intramolecular chelation.[18] Silyl ether derivatives such as **21** would not be expected to participate in additional stabilization of the anion by chelation and introduce additional steric hindrance to nucleophilic attack at Sn. Therefore, transmetalation of **21** by BuLi may not lead to a significantly more stabilized anion and may be impeded by steric factors. Once transmetalation does occur, for stannanes such as **1**, the reverse Brook rearrangement is very fast, precluding the development of any significant concentration of free α-silyloxy carbanion.

The steric limitations to transmetalation can be addressed by changing from Bu to Me alkyl substituents on Sn. Yet, this modification of the reverse Brook procedure also required 3 equiv of BuLi. A trapping experiment was designed to ascertain if BuLi could possibly exchange for methyllithium (MeLi) rather than the α-silyloxy carbanion. MeLi, according to the relative stability scale discussed above, would be slightly more stable than BuLi and of comparable stability to the α-silyloxy carbanion. Reaction of **23** with 3 equiv of BuLi in THF at −78 °C for 15 min followed by the addition of excess benzaldehyde provided three products, **22**, **34**, and **35**. Clearly Bu–Me exchange does occur, but complete reaction of **23** to **21** does not occur. If **21** had been produced,



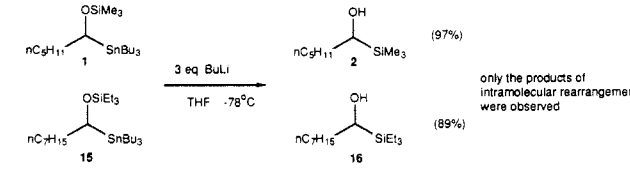
21 would not have transmetalated and rearranged under the reaction conditions and would have been isolated from the reaction mixture. A potential route for the sequential transmetalation and rearrangement process is given in Scheme III. Bu–Me exchange may occur via a short-lived stannylate intermediate **36**. Either BuLi, MeLi, or the α-silyloxy carbanion **39** could be released from intermediate **36**, ultimately generating the product mixture observed. Continued Bu–Me exchange could also produce intermediates **37** and **38** prior to generation of the transient intermediate **39**. GC/MS studies of crude reaction mixtures support the generation of both intermediates **37** and **38** as precursors to **22**. It is important to realize that **37** and **38** may form stannylate intermediates by addition of MeLi or BuLi present in the reaction mixture, and the formation of any stannylate is a reversible process. Therefore, our evidence indicates that the overall rearrangement process is due to the establishment of a complex equilibrium mixture of mixed tetraalkylstannanes and lithio carbanions based on the relative stability of the anions.

The α-silyloxy carbanion **39** must not be significantly more stable than BuLi or MeLi and is only generated in the presence of an excess of the alkyllithium species. Further evidence in support of the relative anion stability argument is given by the results obtained in the transmetalation/rearrangement of stannane **24**. The reverse Brook process provides **25** in 65% yield using the optimized reaction conditions (3 equiv of BuLi). However, only 1 equiv of BuLi is required for rearrangement, resulting in a 67% yield of **25**. The benzylic anion intermediate **40** is considerably



more stable than BuLi, which allows for the establishment of an equilibrium favoring **40** without an excess of BuLi. The reverse Brook rearrangement in all cases is then ultimately driven forward by rearrangement to the more thermodynamically stable lithio alkoxide.

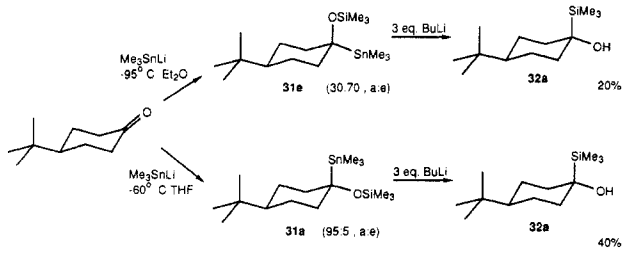
The rapid rearrangement and lack of detectable α-silyloxy anionic intermediates gave an indication that the tin-mediated reverse Brook rearrangement, in analogy to the aryl reverse Brook rearrangement studied by Wright and West,[2a] was an intramolecular reaction. To test this assumption, a cross-over experiment was designed and carried out. Stannanes **1**, **3**, **13**, and **15** were prepared and transformed to the corresponding α-hydroxyalkyl silanes **2**, **4**, **14**, and **16** independently (see Tables I and II). A 1:1 mixture of **1** and **15** was then treated with 3 equiv of BuLi in THF at −78 °C for 15 min. The transmetalation/rearrangement was complete for both stannanes and only the α-hydroxyalkyl silanes **2** and **16** from intramolecular reaction were obtained in 97% and 87% isolated yield, respectively. No trace of the cross-over products **4** or **14** were detected by capillary GC analysis of the crude reaction product mixture.



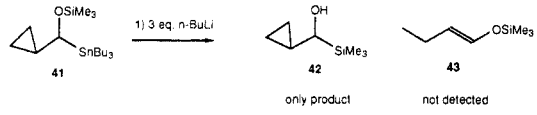
The possibility of a radical process was also examined by using the cyclopropyl-substituted stannane **41**. Cyclopropyl-substituted

(18) The exact nature of α-alkoxy stabilization of organolithio anions is not known. For theoretical calculations on the stability of α-heteroatom-substituted organolithium compounds, see: Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagle, G. W.; Rhode, C.; Arad, D.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 6467–6475.

Scheme IV. Preparation and Rearrangement of Axial and Equatorial Isomers of Stannane **31**

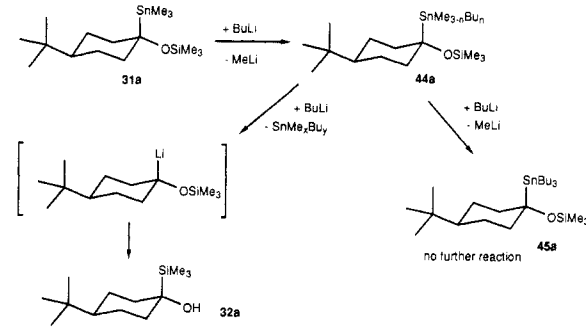


methyl radicals are known to readily undergo ring opening.[19] Oxygen-substituted species that ring open to form an enol ether have also been examined.[20] If the reverse Brook rearrangement pathway involved a radical intermediate, cleavage of the cyclopropane ring to ultimately form the silyl enol ether **43**[21] should occur in preference to formation of alcohol **42**. The silyl enol ether **43** was prepared independently to provide authentic material for comparison to the crude products obtained from the rearrangement reaction mixture. Careful analysis by ^{1}H NMR and capillary GC/MS revealed no trace of **43**, indicating that the rearrangement does not occur via a radical pathway. The very volatile rearranged product **42** was obtained in 45% (GC) overall yield.

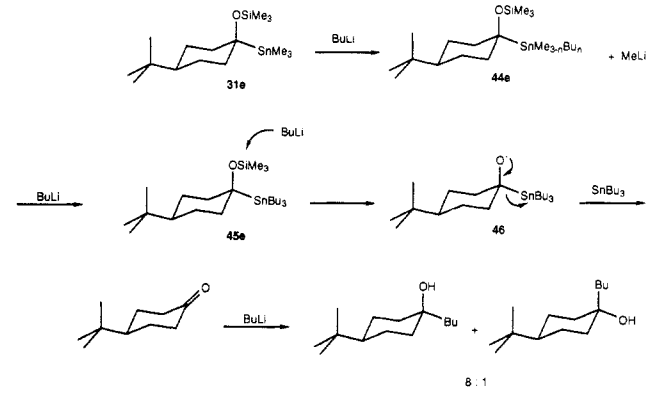


Stereochemistry of the Rearrangement. The stereochemistry of the aliphatic reverse Brook rearrangement for a quaternary carbon was then investigated by using a configurationally fixed stannane derived from 4-*tert*-butylcyclohexanone. McGarvey and co-workers[12c] had demonstrated that (trialkylstannyl)lithium adds to 4-*tert*-butylcyclohexanone under thermodynamic conditions (−60 °C, THF) to provide the axial stannane isomer. The reversible condensation reaction leads to the axial stannane rather than the equatorial isomer in part due to the long C–Sn bond, which effectively reduces potential 1,3-diaxial interactions.[22] The equatorially enriched isomeric mixture can be obtained under kinetic conditions (−95 °C, Et_2O). As illustrated in Scheme IV, a 95:5 axial/equatorial mixture of stannane **31a**/**31e** was prepared by using the thermodynamic reaction conditions described above. Likewise, the equatorially enriched isomer mixture (30:70 of **31a**/**31e**) was obtained by using the kinetic conditions. The thermodynamic and kinetic isomer mixtures of **31** were subjected to the rearrangement conditions (3 equiv of BuLi, −78 °C, THF) independently. Interestingly, a single isomer of the silyl alcohol **32** was obtained from both reactions. The material balance in each case was excellent (>95%), yet the isolated yield of the pure silyl alcohol **32** was 40% from the thermodynamic (axial Sn) mixture and 20% from the kinetic (equatorial Sn) mixture. GC/MS analysis indicated that all of the starting material **31a** and **31e** had been consumed, yet considerable amounts of stannane products were detected. The axial stannane **31a** undergoes Bu–Me exchange, as in the case of stannane **23** described earlier, providing the mixed Me/Bu stannane **44** and the tributylstannane **45**. The axial tributylstannane **45** is inert to the rearrangement reaction conditions; therefore, silane **32a** must arise from **44a** or a stannylate derived from **44a** (Scheme V). The attempted use of MeLi rather than BuLi to affect transmetalation and rearrangement was ineffective and could not be used to circumvent the Bu–Me exchange process. Interestingly, the equatorial stannane **31e** also

Scheme V. Transmetalation and Rearrangement of Stannane **31a**

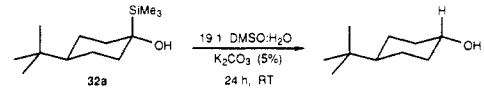


Scheme VI. Fate of the Equatorial Stannane **31e**



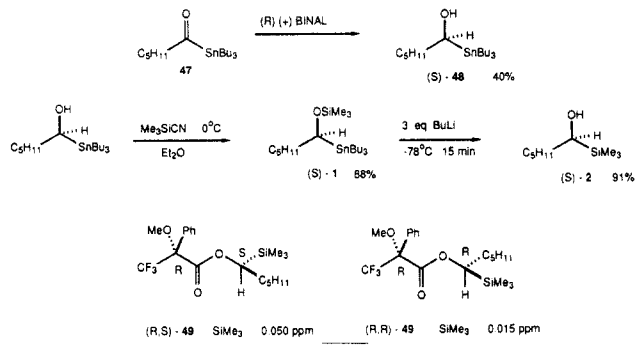
underwent complete conversion to **45e** (through intermediates **44e**); however, **45e** suffered nucleophilic attack at the Si atom of the silyl ether to generate alkoxide **46**. The alkoxide **46** subsequently undergoes reversible addition of (tributylstannyl)lithium, providing 4-*tert*-butylcyclohexanone which is immediately trapped by reaction with the excess BuLi present (Scheme VI). All of the intermediates shown in Schemes V and VI as well as the mixed tetraalkyltin byproducts ($Bu_nMe_{3-n}Sn$) were identified by GC/MS.

The stereochemistry of the single silyl alcohol isomer **32** obtained was unambiguously determined by conversion to 4-*tert*-butylcyclohexanol. The aliphatic forward Brook rearrangement has been studied by Hudrlik and co-workers[23a] and Wilson and co-workers.[23b] Each of these groups determined that quaternary (α-hydroxyalkyl)alkylsilanes undergo the Brook rearrangement with retention of configuration at carbon, in contrast to the inversion at carbon observed for aryl-substituted cases.[1] The silyl alcohol **32** was subjected to the conditions reported by Hudrlik[23a] and resulted in the equatorial alcohol trans isomer of 4-*tert*-butylcyclohexanol.[24] Therefore, the axial stannane **31a** had rearranged stereospecifically to provide the axial silane **32a**, i.e., the aliphatic reverse Brook rearrangement occurs with retention of configuration at carbon. The lower yield of alcohol **32a** obtained from the kinetic isomer mixture compared to the thermodynamic isomer mixture of stannane **31** reflects the smaller amount of axial isomer **31a** initially present. The low overall yield of the rearrangement can also be explained by the lower stability of the tetrasubstituted α-silyloxy anion compared to BuLi or MeLi (Scheme II). It is interesting to note that transmetalation of the axial stannane **31a** leading to the transient axial anion is apparently more favorable than generation of the equatorial anion. An



(19) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734–1736.
(20) Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P. M.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 287–292.
(21) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. O. *J. Org. Chem.* **1969**, *34*, 2324–2336.
(22) Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893–1904.
(23) (a) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809–6811. (b) Wilson, S. R.; Hague, M. S.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 747–748.
(24) Stereochemical assignment verified by direct comparison (GC co-injection) to an authentic sample.

Scheme VII. Synthesis of (*S*)-2 via Reverse Brook Rearrangement



independent synthesis of the equatorial isomer of silane **32e**[25] was achieved via direct addition of Me_3SiLi[7] albeit in very low chemical yield (<10%). Reexamination of capillary GC traces of the crude reaction products from the rearrangement of **31a**/**31e** revealed none of **32e**. While (trialkylstannyl)lithium reagents preferentially add to 4-*tert*-butylcyclohexanone by an axial approach, (trimethylsilyl)lithium reacts like other bulky nucleophiles adding to the carbonyl from an equatorial approach.

Assessment of the aliphatic reverse Brook rearrangement as a potential route to optically active (α-hydroxyalkyl)alkylsilanes was also carried out as shown in Scheme VII. Acyl stannane **47** was prepared from hexanal by the method of Quintard et al.[26] The unstable acyl stannane was reduced by (*R*)-(+)-BINAL,[27] providing the α-hydroxy stannane (*S*)-**48** in 98% ee as determined by ^{19}F NMR analysis of the Mosher ester derivative.[28] Chan and Chong[29a] and Marshall and Gung[29b,c] have independently demonstrated that acyl stannane reduction using (*R*)-(+)-BINAL generates the *S* enantiomer of the α-hydroxy stannane. The configurational integrity of α-alkoxyorganolithio species obtained by transmetalation of α-alkoxyorganostannanes is now well established.[12b,14,29a] Therefore, we presumed that the *S* stannyl alcohol **48** would be converted to the *S* silyl alcohol **2** if the aliphatic reverse Brook rearrangement of (*S*)-**1** occurred without racemization. Silylation of (*S*)-**48** and subsequent rearrangement of (*S*)-**1** provided (*S*)-**2** in 80% overall yield from **48**. Mosher ester preparation via dicyclohexylcarbodiimide coupling and ^{19}F NMR (470 MHz) analysis clearly revealed that the silyl alcohol **2** was obtained in 97% ee. The absolute configuration of **2** was assigned via comparison of the Mosher ester derivative of racemic **2** and the optically pure material. The trimethylsilyl group for each diastereomer derived from (*R*)-Mosher acid was cleanly resolved by ^1H NMR (300 MHz). The *R,S* diastereomer signal appeared at 0.050 ppm and the *R,R* diastereomer at 0.015.[30] The optically active silyl alcohol Mosher ester derivative revealed a singlet at 0.050 ppm for the Me_3Si moiety. Therefore the aliphatic reverse Brook rearrangement had occurred with retention of configuration and without racemization.

Conclusions. The reverse Brook rearrangement can be carried out on aliphatic substrates providing the requisite α-silyloxy carbanion is generated by transmetalation of the appropriate stannane. The novel Sn–Li transmetalation chemistry observed may be explained by the establishment of a complex equilibrium that is dependent on the relative stability of the carbanions. An apparent steric restriction at carbon is overcome by using trimethylstannane derivatives in place of tributylstannane precursors. For the synthesis of (α-hydroxyalkyl)alkylsilanes derived from aldehydes, there is no steric limitation to the alkyl substituents present on silicon; however, only (α-hydroxyalkyl)trimethylsilanes are available from ketones. The functionalized silicon compounds are produced in reasonable overall yields from the three-step sequence.

The rearrangement is an intramolecular process that does not involve radical intermediates. The migration of silicon from oxygen to carbon is extremely facile, preventing attempts to trap an intermediate carbanion with electrophiles. As in the forward Brook rearrangement, these observations also implicate a pentavalent silicon (silicate) intermediate (Scheme I). The stereochemistry of the rearrangement has been clearly defined to occur with retention of configuration at carbon. Therefore, the reverse Brook rearrangement in aliphatic systems bears the same stereochemical result as the aliphatic forward Brook rearrangement, while aryl-substituted species undergo rearrangement in the forward and reverse Brook sense with inversion of configuration at carbon.

Experimental Section

General Procedure for Reverse Brook Rearrangement. (a) **[α-[(Trialkylsilyl)oxy]alkyl]trialkylstannanes.** (Tributylstannyl)lithium or (trimethylstannyl)lithium was prepared by published procedures.[10,11] A THF solution of the stannyl anion (0.95 equiv, 0.1 M concentration) was cooled to −78 °C and the aldehyde (1.0 equiv) was added dropwise. The reaction mixture was stirred at −78 °C for 15 min and then quenched at −78 °C by the dropwise addition of the desired trialkylsilyl cyanide or triflate (1.5 equiv). The mixture was allowed to gradually warm to room temperature and then stirred for 1 h. The solution was then diluted with 100 mL of petroleum ether, washed with 20 mL of saturated aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure to provide the crude stannyl silyl ether.

(b) **Reverse Brook Rearrangement.** The crude stannyl silyl ether was dissolved in 25 mL of dry THF and cooled to −78 °C (under Ar). A hexane solution of *n*-butyllithium (3.0 equiv) was added dropwise via syringe. The reaction mixture was then allowed to stir at −78 °C for 15 min and quenched at −78 °C by the rapid addition of 5 mL of water. After warming to room temperature, the reaction mixture was worked up by extraction using petroleum ether (as described above). The (α-hydroxyalkyl)trialkylsilane product was purified by flash chromatography on silica gel using 100% hexane to first elute the tetraalkylstannane byproduct, followed by a gradient elution using a 1%, 2%, and then 3% ethyl acetate/hexane system.

Variations for O-Silylation. 1-[Dimethyl(3-propen-1-yl)silyl]hexan-1-ol (10). Benzo-15-crown-5 (0.5 g, 2 mmol) was added to a solution of (tributylstannyl)lithium (15 mmol) prior to the addition of the aldehyde (15 mmol). Allyldimethylsilyl chloride (2.69 mL, 20 mmol) was then added in place of the trialkylsilyl cyanide or triflate. The reaction mixture was then allowed to stir at room temperature for 24 h. The reaction mixture was worked up as described above, and the crude product was subjected to the rearrangement conditions. ^1H NMR ($CDCl_3$): δ 0.03 (s, 3 H), 0.04 (s, 3 H), 0.89 (t, 3 H, *J* = 7 Hz), 1.25–1.64 (m, 9 H), 3.40 (t, 1 H, *J* = 7 Hz), 4.93 (m, 2 H), 5.82 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −5.53, −5.22, 14.54, 21.79, 23.18, 27.04, 32.29, 33.99, 65.79, 113.8, 135.6. IR (neat) (cm^{-1}): 3400, 1620, 1450, 1240, 880. Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.98; H, 12.02.

1-(Dimethylphenylsilyl)hexan-1-ol (12). A crude sample of 1-(tributylstannyl)hexan-1-ol (7.82 g, 20 mmol) was dissolved in 25 mL of CH_2Cl_2 and cooled to 0 °C (ice water bath). Diisopropylethylamine (13.0 g, 100 mmol) and 4-(*N,N*-dimethylamino)pyridine (10 mg) were then added, followed by the dropwise addition of chlorodimethylphenylsilane (6.83 g, 40 mmol). The reaction mixture was allowed to gradually warm to room temperature and then stirred at room temperature for 48 h. The reaction mixture was worked up as described in the general procedure, and the crude product was subjected to the rearrangement conditions. ^1H NMR ($CDCl_3$): δ 0.34 (s, 6 H), 0.88 (t, 3

(25) The stereochemistry of the equatorial silyl alcohol was assigned by conversion to axial 4-*tert*-butylcyclohexan-1-ol via the aliphatic Brook rearrangement.[23] The stereochemistry of axial and equatorial stannyl, germyl, and silyl substituents on cyclohexanes may also be assigned by spectral data, see refs 12c, 22, and references therein.

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(30) For references to the assignment of absolute configuration using Mosher ester derivatives, see: Yamaguchi, S. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 1, pp 125–152.

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H, J = 6.6 Hz), 1.26 (m, 6 H), 1.55 (m, 2 H), 3.27 (s, 1 H), 3.52 (t, 1 H, J = 5.1 Hz), 7.39 (m, 3 H), 7.56 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ −5.78, 13.93, 22.49, 26.40, 31.51, 32.15, 55.45, 127.6, 129.0, 134.0, 136.7. IR (neat) (cm^{-1}): 3400, 3025, 1460, 1420, 1245. Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.12; H, 10.23. Found: C, 71.08; H, 10.19.

α-Hydroxyalkyl or Aryl Silanes.[31] **1-(Trimethylsilyl)hexan-1-ol (2).** ^{1}H NMR ($CDCl_3$): δ 0.02 (s, 9 H), 0.88 (t, 3 H, J = 5 Hz), 1.22–1.60 (m, 9 H), 3.28 (t, 1 H, J = 7 Hz). ^{13}C NMR ($CDCl_3$): δ −4.01, 13.94, 22.52, 26.45, 31.73, 33.42, 65.95. IR (neat) (cm^{-1}): 3400, 1640, 1460, 1250. Anal. Calcd for $C_9H_{22}OSi$: C, 61.99; H, 12.72. Found: C, 62.06; H, 12.69.

1-(Triethylsilyl)hexan-1-ol (4). ^{1}H NMR ($CDCl_3$): δ 0.61 (q, 6 H, J = 8 Hz), 0.88 (t, 3 H, J = 7 Hz), 0.98 (t, 9 H, J = 8 Hz), 1.28–1.59 (m, 9 H), 3.44 (dd, 1 H, J = 10 and 2.5 Hz). ^{13}C NMR ($CDCl_3$): δ 2.32, 8.17, 14.73, 23.25, 27.33, 32.40, 34.60, 65.10. IR (neat) (cm^{-1}): 3400, 1640, 1460, 1250. Anal. Calcd for $C_{12}H_{28}OSi$: C, 66.59; H, 13.04. Found: C, 66.68; H, 13.01.

1-[Dimethyl(2-methylpropyl)silyl]hexan-1-ol (6). ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 3 H), 0.02 (s, 3 H), 0.92 (s, 9 H), 0.93 (t, 3 H, J = 7 Hz), 1.30–1.64 (m, 8 H), 3.37 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −3.90, 13.65, 18.65, 22.13, 24.25, 25.41, 26.76, 31.89, 33.89. IR (neat) (cm^{-1}): 3400, 1460, 1250, 910. Anal. Calcd for $C_{12}H_{28}OSi$: C, 66.60; H, 13.04. Found: C, 66.70; H, 12.98.

1-(Tri-2-propylsilyl)hexan-1-ol (8). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3 H, J = 7 Hz), 1.11 (d, 18 H, J = 5 Hz), 1.10–1.50 (m, 9 H), 1.63 (m, 3 H), 3.65 (dd, 1 H, J = 11 and 2.4 Hz). ^{13}C NMR ($CDCl_3$): δ 10.54, 14.06, 18.97, 19.04, 22.72, 27.15, 31.67, 34.68, 64.53. IR (neat) (cm^{-1}): 3400, 1380, 1250. Anal. Calcd for $C_{15}H_{34}OSi$: C, 69.69; H, 13.26. Found: C, 69.76; H, 13.21.

1-(Trimethylsilyl)octan-1-ol (14). ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 9 H), 0.88 (t, 3 H, J = 7 Hz), 1.27–1.53 (m, 13 H), 3.50 (t, 1 H, J = 7 Hz). ^{13}C NMR ($CDCl_3$): δ −3.97, 14.06, 22.62, 26.76, 29.28, 29.51, 31.83, 33.45, 66.05. IR (neat) (cm^{-1}): 3400, 1460, 1250. Anal. Calcd for $C_{12}H_{26}OSi$; C, 65.27; H, 12.95. Found: C, 65.33; H, 12.94.

1-(Triethylsilyl)octan-1-ol (16). ^{1}H NMR ($CDCl_3$): δ 0.61 (q, 6 H, J = 8 Hz), 0.88 (t, 3 H, J = 7 Hz), 0.98 (t, 9 H, J = 7 Hz), 1.28–1.59 (m, 13 H), 3.44 (dd, 1 H, J = 10 and 2.5 Hz). ^{13}C NMR ($CDCl_3$): δ 2.34, 8.22, 14.78, 23.34, 27.70, 30.03, 30.19, 32.58, 34.68, 65.12. IR (neat) (cm^{-1}): 3400, 1460, 1250. Anal. Calcd for $C_{14}H_{32}OSi$: C, 68.66; H, 13.17. Found: C, 68.59; H, 13.17.

3-Phenyl-1-(trimethylsilyl)propan-1-ol (18). ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 9 H), 1.80 (m, 2 H), 2.70 (m, 2 H), 3.39 (t, 1 H, J = 7 Hz), 7.31 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 4.03, 33.29, 35.32, 65.53, 125.79, 128.27, 128.40, 128.47, 142.20. IR (neat) (cm^{-1}): 3400, 3200, 1610, 1490, 1250, 840. Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 69.24; H, 9.72.

Cyclohexyl(trimethylsilyl)methanol (20). ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 9 H), 1.01–1.45 (m, 6 H), 1.49–1.90 (m, 6 H), 3.11 (d, 2 H, J = 5 Hz). ^{13}C NMR ($CDCl_3$): δ 1.83, 23.28, 27.02, 27.18, 30.06, 31.32, 42.89, 72.26. IR (neat) (cm^{-1}): 3400, 1450, 1250. Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.44; H, 11.90. Found: C, 64.52; H, 11.89.

2,2-Dimethyl-1-(trimethylsilyl)propan-1-ol (22). ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 9 H), 0.91 (s, 9 H), 1.80 (s, 1 H), 2.98 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 0.31, 26.99, 28.15, 76.58. IR (neat) (cm^{-1}): 3400, 1350, 1240. Anal. Calcd for $C_8H_{20}OSi$: C, 59.93; H, 12.57. Found: C, 60.00; H, 12.53.

(Triethylsilyl)phenylmethanol (27). ^{1}H NMR ($CDCl_3$): δ 0.21–1.25 (m, 15 H), 1.52 (s, 1 H), 4.54 (s, 1 H), 7.23 (s, 5 H). ^{13}C NMR ($CDCl_3$): δ 1.30, 7.28, 68.73, 124.85, 125.66, 128.15. IR (neat) (cm^{-1}): 3400, 3100, 2900, 1710, 1600, 1240. Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 69.97; H, 10.05.

1-(Trimethylsilyl)cyclohexanol (29). ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 9 H), 1.35–1.6 (m, 10 H), 2.35 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 4.06, 20.69, 26.73, 33.52, 65.96. IR (neat) (cm^{-1}): 3490, 2930, 2870, 1245. Anal. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70. Found: C, 62.90; H, 11.65.

4-(2-Methylpropyl)-1-(trimethylsilyl)cyclohexanol (32a). ^{1}H NMR ($CDCl_3$): δ 0.17 (s, 3 H), 0.76 (s, 9 H), 0.83–1.24 (m, 8 H), 1.24 (s, 1 H), 1.59 (d, 1 H, J = 10 Hz), 2.02 (d, 1 H, J = 11 Hz). ^{13}C NMR ($CDCl_3$): δ −2.25, 25.58, 27.44, 32.17, 38.48, 47.42, 67.26. IR (CCl_4) (cm^{-1}): 3400, 1450, 1310, 1270. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.27; H, 12.30.

Trapping Experiments. Transmetalation of 21 and 23. Stannane **21** (1.0 equiv) was subjected to the normal rearrangement conditions (3 equiv of BuLi at −78 °C) for 15 min. Benzaldehyde (3 equiv) was then added (neat), and the mixture was stirred for 5 min before aqueous workup as described in the general procedure for the reverse rearrangement. Stannane **23** was similarly treated. The reaction products were isolated and identified by ^{1}H NMR and comparison by GC with authentic samples.

Cross-Over Experiment. Samples of stannane **1** (232 mg, 0.5 mmol) and stannane **15** (256 mg, 0.5 mmol) were combined and dissolved in 25 mL of THF. The solution was cooled to −78 °C (CO_2/acetone), and a hexane solution of BuLi (1.18 mL of a 2.5 M solution) was then added dropwise via syringe. The reaction mixture was stirred at −78 °C for 15 min and then quenched by the rapid addition of 5 mL of saturated aqueous ammonium chloride. The reaction mixture was worked up as described in the general procedure. The crude product mixture was examined by capillary GC prior to chromatographic separation of the products.

Radical Intermediate Experiment. Stannane **41** was prepared as described in the general experimental section from cyclopropanecarboxaldehyde.

Cyclopropyl(tributylstannyl)methanol (41). ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 9 H), 0.08 (m, 2 H), 0.20 (m, 1 H), 0.46 (m, 1 H), 0.58 (m, 1 H), 0.87 (t, 9 H, J = 6 Hz), 1.20–1.60 (m, 18 H), 3.30 (d, 1 H, J = 10 Hz). ^{13}C NMR ($CDCl_3$): δ 0.92, 3.63, 8.93, 9.75, 14.39, 19.27, 28.25, 29.96, 74.25.

Rearrangement of **41** was effected by the standard procedure. The crude reaction product was carefully examined by capillary GC for any trace of enol ether **43**. Only the rearranged prod ct, **42**, was detected. GC/MS (chemical ionization) analysis of **42** revealed the molecular ion (M^+, 144), loss of CH_3 (129), and loss of OH (127). The enol ether **43** mass spectrum was clearly distinct from that of **42**.

Cyclopropyl(trimethylsilyl)methanol (42). ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 9 H), 0.01–0.85 (m, 5 H), 2.50 (d, 1 H, J = 11 Hz). IR (CCl_4) (cm^{-1}): 3400, 3075, 1455, 1248, 1065. (No trace of enol ether C=C stretch at 1655 cm^{-1}.)

Stereochemical Studies. 4-*tert*-Butylcyclohexanone. Axial and equatorial isomers of stannane **31** were prepared by trimethylsilyl cyanide O-silylation of the corresponding alcohols obtained according to the procedure of McGarvey et al.[12c] The stannanes **31a** and **31e** were subjected to the normal rearrangement conditions followed by aqueous workup. Complete separation of axial and equatorial isomers of **44** was achieved by capillary GC. Each compound was identified by GC/MS (molecular ion and fragmentation) analysis by using EI and CI methods. An authentic sample of 1-*n*-butyl-4-*tert*-butylcyclohexanol was prepared by direct addition of BuLi to 4-*tert*-butylcyclohexanone. The butyl addition byproducts were then identified by GC co-injection. The equatorial isomer **32e** was prepared by direct addition of (trimethylsilyl)lithium (from hexamethyldisilane) to 4-*tert*-butylcyclohexanone.[11] Stereochemical proof was obtained by conversion of **32a** to equatorial 4-*tert*-butylcyclohexanol via a normal Brook rearrangement using 5% K_2CO_3 in 19:1 DMSO/H_2O (24 h, room temperature).[23] Silane **32e** was converted to axial 4-*tert*-butylcyclohexanol by the same procedure.

Stereochemical Studies. Asymmetric Synthesis. Acylstannane **47** was prepared as described by Quintard et al.[26] Reduction using (*R*)-(+)-BINAL[29a,c] provided the *S* stannane **48** in 40% yield after chromatography. A small quantity (62 mg) of **48** was converted to the Mosher ester derivative by using (*R*)-(+)-MTPA, DCC, and DMAP.[29c] The remainder of pure **48** was directly converted to the silyl ether (*S*)-**1** by reaction with 1.1 equiv of trimethylsilyl cyanide in ether (room temperature, 8 h) (88% yield). The silyl ether obtained required no purification and was directly subjected to the rearrangement conditions. The optically active (*S*)-**1** was obtained in 91% yield. The silyl alcohol (*S*)-**1** was converted to the Mosher ester derivative by using (*R*)-(+)-MTPA as described above. (*R*)-(+)-MTPA ester of (*S*)-**48**: ^{19}F NMR ($CDCl_3$) δ −71.69 (s, relative integration 98%), −71.54 (s, relative integration 2%). (*R*)-(+)-MTPA ester of (*S*)-**1**: ^{19}F NMR ($CDCl_3$) δ −71.66 (s, relative integration 97%), −71.39 (s, relative integration 3%).

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