

showed 50% conversion of **2a** to **1a** in the first tube, 53% in the second.

$\alpha$ -Mercapto- $\alpha$ -trimethylgermyltoluene (**2b**) was isomerized in the same fashion to **1b**. Rearrangement was first order in **2b**,  $t_{1/2} = 3$  min.

#### Radical Rearrangement of $\alpha$ -Mercapto- $\alpha$ -trimethylsilyltoluene

(**2a**). **2a** (250 mg, 1.3 mmol) was heated to 100° in heptane in the presence of azobisisobutyronitrile (17 mg, 0.2 mmol). Glc analysis after 37 min showed 92% isomerization to benzylthiotrimethylsilane (**1a**) had occurred.

**2b** was isomerized in the same fashion to **1b**, 96% isomerization occurring after 10 min.

## New Anionic Rearrangements. XIX. Stereochemistry of the Alkoxysilane to Silylcarbinol Anion Rearrangement<sup>1-3</sup>

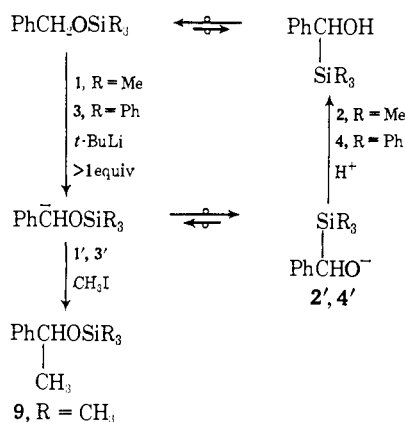
Antony Wright<sup>4</sup> and Robert West\*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received September 7, 1973

**Abstract:** Metalation of *S*-(+)-benzyl- $\alpha$ -*d*-oxytrimethylsilane (*S*-(+)-**5**) with excess *tert*-butyllithium at -50° occurs rapidly at benzyl carbon with a hydrogen/deuterium isotope ratio  $k_H/k_D = 24 \pm 4$ , the highest value ever reported for a metalation reaction. The resulting carbanion undergoes a rapid intramolecular rearrangement to the oxyanion of *S*-(-)- $\alpha$ -hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -*d*-toluene (*S*-(-)-**6**). Acidification of the anion solution yields the silylcarbinol *S*-(-)-**6**. Rearrangement occurs stereospecifically with 99% inversion at benzyl carbon, showing that silicon migrates very rapidly to the benzyl carbanion center. The anion of *S*-(-)-**6** racemizes slowly at 25° and reacts with methyl iodide to give the unrearranged totally racemic derivative 1-phenyl-1-trimethylsiloxyethane-1-*d*. Racemization of the anion thus appears to occur by equilibration with the carbanion isomer. *S*-(+)-Benzyl- $\alpha$ -*d*-oxytrimethylgermane and *S*-(+)-benzyl- $\alpha$ -*d*-oxytriphenylsilane also rearrange with inversion of configuration at carbon. Analysis of *S*-(-)-**6** for isotopic and optical purity was performed by nmr spectroscopy in the presence of tris(3-heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III). This chiral shift reagent shows simultaneously both an isotope effect and an enantiomeric effect in the magnitude of resonance displacement.

We have reported<sup>5</sup> that benzyloxytrimethylsilane, upon metalation at the benzyl carbon atom with excess *tert*-butyllithium at -78°, undergoes a rapid intramolecular isomerization to the anion of the silylcarbinol  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**1**  $\rightarrow$  **2'**, Scheme I). Whereas protonation of the anion **2'** gives

Scheme I



the silylcarbinol **2**, methylation of the anion with methyl iodide at 25° slowly gives **9**, which is derived from the unrearranged carbanion **1'**. The alkoxysilane

to silylcarbinol anion rearrangement is formally analogous to the classical Wittig rearrangement of metalated benzyl ethers to anions of secondary alcohols.<sup>6</sup> However, its mechanism appears to be more closely related to that of the Brook rearrangement, in which silylcarbinols rearrange to alkoxysilanes under base catalysis.<sup>7,8</sup>

We sought to use some of the same techniques to study the anion rearrangement as have been used to study the Brook rearrangement, hoping thereby to make an explicit comparison of their mechanisms. Recently Biernbaum and Mosher,<sup>9</sup> in an elegant study, proved that the catalytic rearrangement proceeds stereoselectively with 90–100% inversion of configuration at benzyl carbon, not retention as had been previously supposed<sup>11</sup> (Scheme II). It seemed possible to use this system in reverse in order to elucidate the stereochemistry of the anion rearrangement.

#### Rearrangement of *S*-(+)-Benzyl- $\alpha$ -*d*-oxytrimethylsilane

Because of its ease of metalation, *S*-(+)-benzyl- $\alpha$ -*d*-oxytrimethylsilane (*S*-(+)-**5**) was more convenient to study initially than the triphenylsilyl analog *S*-(+)-**7**. The *S* configuration has been assigned to (+)-benzyl-

(6) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

(7) A. G. Brook, G. E. Legrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967).

(8) A. G. Brook, *Accounts Chem. Res.*, in press.

(9) M. S. Biernbaum and H. S. Mosher, *J. Amer. Chem. Soc.*, **93**, 6221 (1971). Inversion at carbon was also recently observed in an independent study by A. G. Brook.<sup>10</sup>

(10) A. G. Brook and J. D. Pascoe, *J. Amer. Chem. Soc.*, **93**, 6224 (1971).

(11) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

(1) This work was supported in part by the Air Force Office of Scientific Research (NC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR 70-1904.

(2) Previous paper in this series: A. Wright and R. West, *J. Amer. Chem. Soc.*, **96**, 3222 (1974).

(3) Presented in part at the Third International Symposium on Organosilicon Chemistry, Madison, Wis., August 1972.

(4) Procter and Gamble Fellow, 1972–1973.

(5) A. Wright and R. West, *J. Amer. Chem. Soc.*, **96**, 3214 (1974).

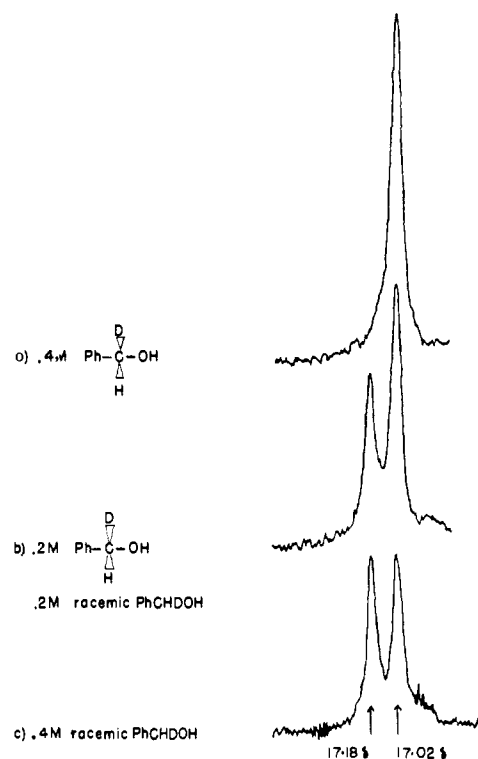
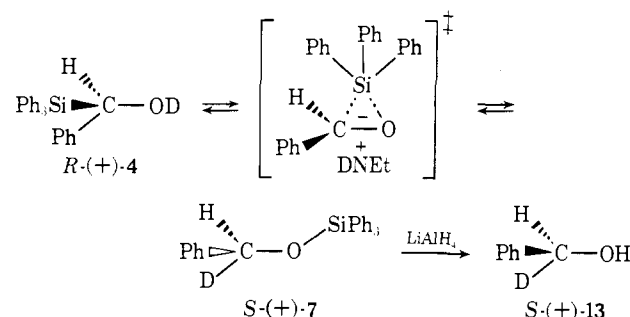


Figure 1. Nmr spectra (100 MHz) of  $\text{CCl}_4$  solutions 0.4 M in  $\text{Eu}(\text{Rf})_3$  and 0.4 M in (a)  $S$ -(+)-**13**, (b) 1:1  $S$ -(+)-**13** and racemic **13**, and (c) racemic **13**.

#### Scheme II



$\alpha$ -*d* alcohol ( $S$ -(+)-**13**).<sup>12,13</sup> Benzaldehyde- $\alpha$ -*d*, reduced conveniently in a rapidly fermenting yeast solution, gave  $S$ -(+)-**13**,<sup>12</sup>  $[\alpha]^{24\text{D}} + 1.46 \pm 0.01$  (neat,  $l = 1$ ). The degree of monodeuteration, determined by mass spectrometry, was  $94.3 \pm 0.7\%$ . The calculated rotation, corrected for incomplete monodeuteration, was  $[\alpha]^{24\text{D}} + 1.54 \pm 0.02$ , which compares well with the maximum reported literature value<sup>12</sup> of  $[\alpha]^{24\text{D}} + 1.58 \pm 0.01$  (neat,  $l = 1$ ). There is no proof, however, that this latter rotation was measured using optically pure sample.<sup>13</sup> We find, however, that the nmr spectrum of  $S$ -(+)-**13** in the presence of the chiral shift reagent<sup>14</sup> tris(3-heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III)<sup>15</sup> shows only one benzyl proton resonance,<sup>16</sup> whereas racemic **13**, prepared by

(12) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Amer. Chem. Soc.*, **88**, 3595 (1966).

(13) D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969).

(14) G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, **92**, 6979 (1970).

(15) H. L. Goering, J. N. Eikenberry, and G. S. Koerner, *J. Amer. Chem. Soc.*, **93**, 5913 (1971).

(16) The AB Quartet<sup>17</sup> due to the enantiotopic protons of the benzyl alcohol impurity present was not observed.

(17) R. R. Fraser, M. A. Petit, and M. Miskow, *J. Amer. Chem. Soc.*, **94**, 3253 (1972).

metal hydride reduction of benzaldehyde- $\alpha$ -*d*, gives two equally intense benzyl proton resonances at  $\delta$  17.02 and 17.18 (Figure 1). Thus the isolated sample of  $S$ -(+)-**13** was optically pure.<sup>18</sup> This is apparently the first reported example of a chiral shift reagent separating resonances due to isomers enantiomeric by virtue of deuterium substitution. The shift difference is not due to the  $S$  and  $R$  enantiomers being complexed to a different degree with europium but rather to the existence of two diastereotopic proton positions at the prochiral<sup>13</sup> benzyl carbon center in the alcohol shift reagent complex.<sup>17,19</sup>

The alkoxyisilane  $S$ -(+)-**5** was prepared from the highly deuterated optically pure  $S$ -(+)-**13**. A small portion of  $S$ -(+)-**5** was reductively cleaved with lithium aluminum hydride<sup>20</sup> to give back **13**, which still exhibited a single benzyl proton resonance in the presence of chiral shift reagent. This proves that no racemization could have occurred during the silylation.

The alkoxyisilane to silylcarbinol anion rearrangement of  $S$ -(+)-**5** dissolved in tetrahydrofuran (THF) was effected by adding excess *tert*-butyllithium at  $-78^\circ$ , warming to  $-50^\circ$  over a 2-min period, and injecting glacial acetic acid at  $-78^\circ$ . Glc analysis showed 73% conversion to  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -*d*-toluene (**6**). After purification by preparative gas chromatography **6** gave an uncorrected rotation of  $[\alpha]^{24\text{D}} - 85.70 \pm 0.02$  ( $l = 1$ , neat)! The high negative rotation at once shows that the rearrangement is highly stereoselective. The absolute configuration of (-)-**6** is assigned as follows. (+)- $\alpha$ -Deuteroxy- $\alpha$ -triphenylsilyl-toluene ((+)-**4**) is known to have the configuration  $R$  from the X-ray determined crystal structure of its *p*-bromobenzoate ester.<sup>21</sup> (+)-**2** has the same configuration as  $R$ -(+)-**4**,<sup>22</sup> and (+)-**6** must have the same configuration as  $R$ -(+)-**2**.<sup>23</sup> Therefore (-)-**6** has the configuration  $S$  and rearrangement proceeds with inversion of configuration at benzyl carbon (Scheme III).

The degree of monodeuteration of **6** cannot be determined accurately in the mass spectrometer because of excessive fragmentation, even at low voltage. Accurate nmr integration shows, however, that **6** is  $90.58 \pm 0.45\%$  monodeuterated. Since **5** is  $94.33 \pm 0.68\%$  monodeuterated, proton transfer occurred much more easily than deuterium transfer in the metalation step. The isotope ratio  $k_{\text{H}}/k_{\text{D}}$  is  $24 \pm 4$ . This value has been subsequently confirmed in a study of the temperature dependence of  $k_{\text{H}}/k_{\text{D}}$  in the metalation of racemic **5**, 99.4% monodeuterated.<sup>24</sup>

Although hydrogen/deuterium isotope ratios have been measured for many proton transfer reactions,<sup>25</sup>

(18) However, the  $R$ -(−) enantiomer, if present in less than 3%, would probably escape detection.

(19) The resonances of the phenyl protons of racemic **13** are not doubled, consistent with the latter shift mechanism.

(20) Attack occurs at silicon to give  $\text{Me}_3\text{SiH}$  and benzyl alcohol; see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

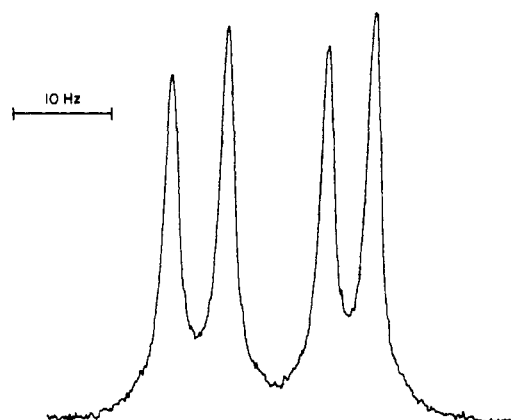
(21) K. Black and H. Hope, *J. Amer. Chem. Soc.*, **93**, 3053 (1971).

(22) M. S. Biernbaum and H. S. Mosher, *J. Org. Chem.*, **36**, 3168 (1971).

(23) The two compounds differ only by virtue of deuterium substitution at the benzylic position. Since the optical rotation of  $S$ -(+)-**5** is only  $[\alpha]^{24\text{D}} + 1.66$ , it is certain that  $R$ -(+)-**2**,  $[\alpha]^{24\text{D}} + 93 \pm 1.5$  (neat)<sup>22</sup> and  $R$ -(+)-**6** have the same configuration.

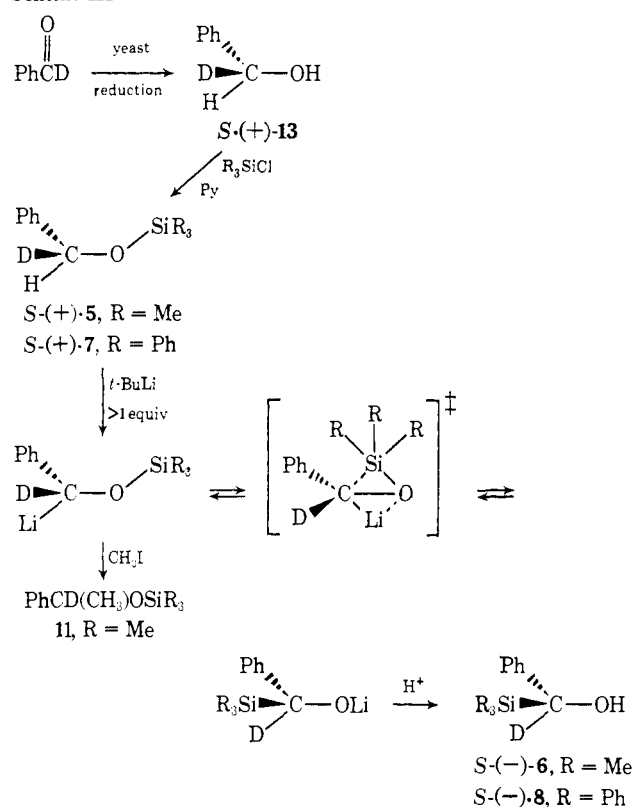
(24) We find  $E_{\text{H}}^\ddagger - E_{\text{D}}^\ddagger = 2.11 \pm 0.1$  kcal/mol between  $-25$  and  $-52^\circ$ , suggesting quantum mechanical tunneling.<sup>25</sup> A. Wright, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1973.

(25) E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).



**Figure 2.** Spectrum (100 MHz) of a  $\text{CCl}_4$  solution 0.4  $M$  in  $\text{Eu}(\text{Rf}^*)_3$ , 0.27  $M$  in racemic  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**2**), and 0.23  $M$  in racemic  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -*d*-toluene (**6**). Assignment of peaks is the same as illustrated in Figure 3.

### Scheme III



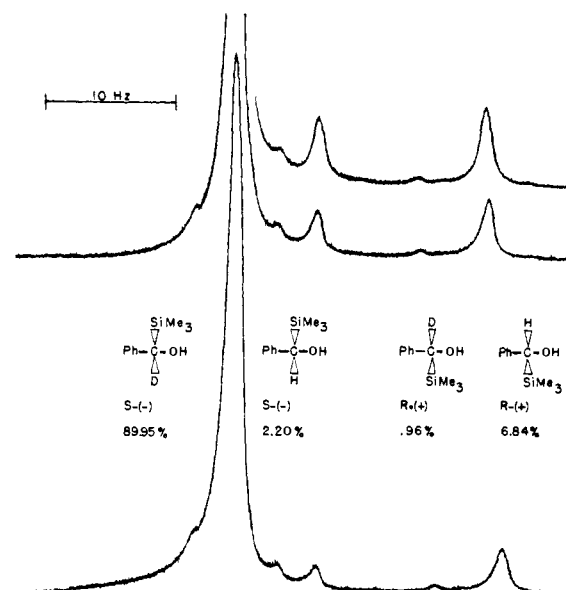
there are apparently only a few examples known where a metal alkyl is the base,<sup>26</sup> only one where *tert*-butyllithium is used,<sup>27</sup> and none studied using metal alkyls at low temperature. This isotope ratio is the highest ever reported in a metalation reaction and one of the highest reported for a proton transfer reaction. The observation of a high hydrogen/deuterium isotope ratio at low temperature has theoretical basis.<sup>28</sup>

The amounts of the various isomeric molecules present in the silylcarbinol product were evaluated by nmr using the chiral shift reagent. For reference, the spectrum of a  $\text{CCl}_4$  solution, 5  $M$  in chiral shift reagent,

(26) J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

(27) D. A. Shirley and J. P. Hendrix, *J. Organometal. Chem.*, **11**, 217 (1968).

(28) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.



**Figure 3.** Spectrum (100 MHz) of a  $\text{CCl}_4$  solution 0.4  $M$  in  $\text{Eu}(\text{Rf}^*)_3$  and 0.5  $M$  in  $S$ -(-)- $\alpha$ -hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -*d*-toluene ( $S$ -(-)-**6**) containing isomeric impurities. Upper traces: same spectrum but with small amounts of racemic  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**2**) added.

0.27  $M$  in racemic **2**, and 0.23  $M$  in racemic **6**,<sup>29</sup> was recorded (Figure 2). The trimethylsilyl resonance is shifted 3 ppm downfield and is split into four separate peaks. The more intense pair of peaks (2nd and 4th from left in Figure 2) is assigned to the two enantiomers of **2**, the undeuterated isomer of **6**. **6** itself gives a pair of resonances shifted 1.8 to 2.4% downfield from the pair due to **2**.<sup>30</sup> To our knowledge this is the first reported example wherein a shift reagent shows simultaneously both an isotope effect and an enantiomeric effect in the magnitude of resonance displacement.

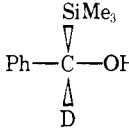
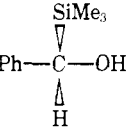
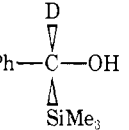
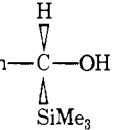
When the silylcarbinol product was subjected to similar nmr analysis, four trimethylsilyl resonances were obtained consisting of a major peak with Si<sup>29</sup> side bands, obviously due to  $S$ -(-)-**6**, and three minor upfield peaks (Figure 3). These can be identified by successive additions of racemic **2**, which cause two of the three peaks to grow in intensity. The intensities (per cent of total) of each peak, measured by direct spectrometer integration, are displayed in Figure 3 and Table I. These data show 90.91% nondeuterated carbinol to be present. This compares favorably with the value 90.58% found by nmr analysis of the silylcarbinol alone. 92.10% of the carbinol is (-) enantiomer and 7.8% is (+) enantiomer. Dividing the observed optical rotation by 0.843, the fraction of excess (-) enantiomer, gives the calculated optical rotation for pure  $S$ -(-)-**6**,  $[\alpha]^{24\text{D}} -102 \pm 1$  (neat).<sup>31</sup>  $S$ -(-)-**6** and  $R$ -(+)-**6** must arise from proton abstraction from **5**. Assuming **5** to be pure  $S$ -(+), 99% inversion must occur.  $S$ -(-)-**2** and  $R$ -(+)-**2** can be formed either by deuterium abstraction from **5** or by proton abstraction

(29) Prepared from racemic **13** via rearrangement of racemic **5**.

(30) Typically, in the presence of achiral shift reagent,  $\alpha$ -deuterated alcohols show resonances shifted 1.4–4.3% further downfield than those of their nondeuterated isomers; see G. V. Smith, W. A. Boyd, and C. C. Hinckley, *J. Amer. Chem. Soc.*, **93**, 6319 (1971).

(31) Although pure  $S$ -(-)-**2**  $[\alpha]^{24\text{D}} -93 \pm 1.5$  (neat)<sup>22</sup> and pure  $S$ -(-)-**6** have slightly different rotations, the error induced in the calculation is negligible.

**Table I.** Composition of Silylcarbinol Isolated from Rearrangement of *S*-(+)-Benzyl- $\alpha$ -*d*-oxytrimethylsilane (*S*-(+)-5)

				
	<i>S</i> -(+)-6	<i>S</i> -(+)-2	<i>R</i> -(+)-6	<i>R</i> -(+)-2
		<i>S</i> -(+)-6	<i>R</i> -(+)-6	<i>R</i> -(+)-2
Metalation occurred at	H	D	H	D
Stereochemistry	Inv	Ret	Ret	Inv
% of total (from Figure 3)	89.95	2.25	0.96	6.84
% from <i>S</i> -(+)-5	89.95	0.05	0.96	4.64
% from <b>1</b>	0.0	2.20	0.00	2.20

from **1**, present as an impurity. Assuming 99% inversion, the former process should produce only  $0.01 \times 6.84 = 0.07\%$  *S*-(+)-2. Thus the 2.25% *S*-(+)-2 actually obtained must arise mainly from **1**. Of course 2.18% of *R*-(+)-2 must also be due to **1**, indicating that the starting alkoxysilane was 95.6% monodeuterated. The mass spectrometrically determined value was 94.33%.

Although the benzyl carbanion **5'** must invert rapidly between enantiomeric forms,<sup>32,37</sup> *S*-(+)-6 is formed from *S*-(+)-5 without racemization occurring. An optically active product can be obtained only if the initial deprotonation produces a very short-lived carbanion. Migration of silicon from oxygen to carbon must therefore occur very quickly.

Although methyl iodide derivatization experiments have shown **1'** and **2'** to be in equilibrium, nmr analysis of the anion solution has shown that **2'** is the predominant species present.<sup>5</sup> When *S*-(+)-5 was metalated at  $-78^\circ$  and the resulting anion solution held 20 hr at  $-40^\circ$  before addition of acetic acid, the percentage of *R*-(+)-6 in the product increased to 4.9%, indicating 9.8% racemization of the anion *S*-(+)-6'. The anion solution did not react appreciably with methyl iodide at  $-40^\circ$ , but methylation did take place at  $25^\circ$ . A freshly prepared anion solution containing excess methyl iodide was warmed to  $25^\circ$  for 13 min, then recooled to  $-78^\circ$  and protonated, yielding an oil consisting of 40 parts 100% racemized 1-phenyl-1-trimethoxysiloxyethane-1-*d* (**11**) and 60 parts 59% racemized **6**. Repeating the experiment without the methyl iodide resulted in the isolation of 100 parts 11% racemized **6**. Apparently the methyl iodide or lithium iodide present in the former experiment increases the rate of racemization of unreacted anion, *S*-(+)-6'. In the former experiment a total of 75% of *S*-(+)-5 is converted to

(32) The benzyl carbon atom in benzyllithium is  $sp^2$  with some  $sp^3$  character.<sup>33</sup> The crystal structure of benzyllithium triethylenediamine complex shows a  $\pi$ -allyl-type coordination between part of the benzyl group and lithium,<sup>34</sup> which is very similar to that in  $CH_3C_6H_4CH_2MoCp(CO)_2$ .<sup>35</sup> (*i*-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>MoCp(CO)<sub>2</sub> undergoes the equivalent of inversion at benzyl carbon rapidly on the nmr time scale.<sup>36</sup>

(33) L. D. McKeever and R. Waack, *J. Organometal. Chem.*, **28**, 145 (1971).

(34) S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Amer. Chem. Soc.*, **92**, 1150 (1970).

(35) F. A. Cotton and M. P. LaPrade, *J. Amer. Chem. Soc.*, **90**, 5418 (1968).

(36) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 1339 (1969).

(37) G. M. Whitesides and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 4878 (1965).

racemic compounds, while 40% is converted to **11**. It appears likely that racemization of **6'** involves the carbanion **5'**. If every time a molecule of **6'** converts to **5'** it loses its preferred configuration, there is a  $(40/75) \cdot 100 = 53\%$  chance that the molecule of **5'** produced will also undergo reaction with methyl iodide. If so the conversion **6'**  $\rightarrow$  **5'** must occur only very slowly at  $25^\circ$ . Alternatively, it is possible that interconversion between **6'** and **5'** occurs many times before either loss of preferred configuration or reaction with methyl iodide occurs, but if so, the anion **5'** must have a very short lifetime. The latter process is consistent with the observed absence of racemization of **5'** when generated by the reaction of *tert*-butyllithium with **5**.

To show that the isomer **5'** would indeed invert rapidly if it had a long lifetime in solution, the metalation of *S*-benzyl- $\alpha$ -*d* methyl ether was conducted. It is known that whereas benzyl methyl ether is rapidly metalated at  $-78^\circ$  in THF, subsequent migration of the methyl group occurs only over an 11-hr period at this temperature.<sup>38</sup> We find that addition of methyl iodide at  $-78^\circ$  to a solution of the optically active ether (*S*)-benzyl- $\alpha$ -*d* methyl ether only 85 sec after addition of excess *tert*-butyllithium gives rapid reaction to produce racemic 1-phenylethyl-1-*d* methyl ether. In fact, racemization likely occurs within several milliseconds of metalation. The rapidity of methyl iodide derivatization here and the extreme slowness of methyl iodide derivatization in the silylcarbinol anion solution at  $25^\circ$  suggest that very little **5'** is present in the silylcarbinol solution.

#### Other Rearrangements

The germanium analog to **5**, *S*-(+)-benzyl- $\alpha$ -*d*-oxytrimethylgermane, was found to rearrange with 98% inversion of configuration at carbon, as determined from the nmr spectrum of the  $\alpha$ -germylcarbinol product with chiral shift reagent. This spectrum, like the spectrum of the silylcarbinol, exhibits the predominant resonance at the farthest downfield position. The isotope ratio,  $k_H/k_D$ , is over 25. From the optical rotation of the product  $[\alpha]^{24D} - 82.1 \pm 0.1$  [*c* 12.6,  $CHCl_3$ ], the rotation of pure *S*-(+)- $\alpha$ -hydroxy- $\alpha$ -trimethylgermyl- $\alpha$ -*d*-toluene is calculated to be  $[\alpha]^{24D} - 96.2 \pm 1$  ( $CHCl_3$ ).

Metalation of the benzyloxytriphenylsilane *S*-(+)-7 occurs slowly during 20 hr at  $-40^\circ$ . The deuterated rearrangement product, isolated upon acid quenching, consists of a mixture of 53 parts *S*-(+)-8 and 47 parts *R*-(+)-8. The net stereochemistry is, again, inversion. The degree of racemization (93%) is much greater than the 10% observed for the anion **6'**, left 20 hr at  $-40^\circ$ . The isotope ratio,  $k_H/k_D$ , is about  $18 \pm 3$ .

#### Mechanisms

**Comparison with the Brook Rearrangement.** An example of the Brook rearrangement of silylcarbinols to alkoxysilanes is the conversion of **2** to **1** which occurs rapidly upon addition of much less than 1 equiv of liquid sodium-potassium alloy, or slowly upon addition of a little of the anion **2'**.<sup>5</sup> A similar catalytic rearrangement occurs rapidly when *S*-(+)-6 is treated with sodium-potassium alloy in ether, producing mainly *S*-

(38) H. Schäfer, U. Schöllkopf, and D. Walter, *Tetrahedron Lett.*, 2809 (1968).

(+)-**5** according to analysis of the benzyl- $\alpha$ -*d* alcohol obtained from subsequent lithium aluminum hydride cleavage. The rearrangement step proceeds with 51% inversion and 49% racemization.

Since both the anion and Brook rearrangements occur with inversion of configuration at carbon, it seems likely that they both proceed through similar transition states. The proposed<sup>7</sup> transition state for the Brook rearrangement is illustrated in Scheme II. The presence of a pentacoordinate silicon atom in a three-membered ring is suggested by the fact that rearrangement occurs with retention of configuration at optically active *silicon*.<sup>11</sup> A kinetic study of the Brook rearrangement using amine catalysts and para-substituted triorganosilylphenylcarbinols has given Hammett reaction constant ( $\rho$ ) values between +3.6 and +4.6, showing that the transition state has considerable negative charge dispersed into the phenyl ring<sup>7</sup> and therefore that there is considerable negative charge at the benzyl carbon atom.

There is no *a priori* requirement that proton free anions, similar either to **1'** or **2'**, be precursors to the transition state in the Brook rearrangement. The proton, although "carried" through the isomerization by the base catalyst, may still be partly bonded to at least one of the two atoms between which it is migrating (O and C) during the entire rearrangement process. This mechanism is consistent with the observation of a very high negative entropy of activation in the rearrangement ( $\Delta S^\ddagger = -35$  to  $-45$  eu).<sup>7</sup>

Our proposed transition state for the anion rearrangement is illustrated in Scheme III. It differs from the transition state in the Brook rearrangement in that no hydrogen bonding proton is available. Since the energy of the transition state is closer to that of **5'** than to **6'**,<sup>5</sup> its geometry should be such that silicon is closer to oxygen than to carbon but lithium closer to carbon than to oxygen. The proposed transition state is not likely to become a true intermediate, since the near 60° SiCO and SiOC bond angles would probably destabilize the transition state more than it is stabilized by pentacoordinate bonding to silicon. The abstraction of the proton and the movement of the silicon atom into the bridging position may be almost concerted. Prior coordination of lithium in *tert*-butyllithium with the siloxy oxygen atom may have properly positioned the silicon atom for entrance to the bridging position even before proton abstraction.

## Experimental Section

Nmr spectra were recorded on Varian HA-100, Varian XL-100, and JEOL MH-100 spectrometers, using CCl<sub>4</sub> as solvent and locking internally on tetramethylsilane (TMS). Gas-liquid chromatographic (glc) separations were made on a Varian Aerograph A-700 chromatograph using columns packed with SE-30 silicone on Chromosorb W. All liquid products were characterized after purification by preparative glc, and yield analyses were based on the areas under glc peaks. Mass spectra were obtained using an AEI Model MS-9 spectrometer. Optical rotations were measured on a Perkin-Elmer model 141 electronic polarimeter which reads to 0.001° in center filled thermostated tubes.<sup>39</sup> All melting and boiling points are uncorrected. *tert*-Butyllithium, 1.27 M in pentane, was obtained from Foote Mineral Co., New Johnsonville, Tenn. Tetrahydrofuran (THF) was dried by distillation from lithium aluminum hydride just prior to use. Camphor-*d* was obtained from Eastman Kodak Co. Heptafluorobutanoyl chloride was obtained from

Pierce Chemical Co., Rockford, Ill. Where prepared previously,<sup>5</sup> compounds were identified by nmr and by the matching of glc retention times on at least two different columns with those of an authentic specimen.

**3-Heptafluoropropylhydroxymethylene-*d*-camphor**<sup>15</sup> (**14**). In an improved procedure, *tert*-butyllithium (158 ml pentane solution, 0.2 mol) was added to camphor-*d* (30.5 g, 0.2 mol) in 158 ml of THF at  $-78^\circ$ . After 15 min, heptafluorobutanoyl chloride (23.2 g, 0.1 mol) was slowly added. The solution was warmed to  $25^\circ$  and after 5 hr 200 ml of dilute aqueous acetic acid and 100 ml of pentane were added. The organic layer was separated and evaporated to dryness. Excess camphor was removed as follows.<sup>40</sup> Cupric acetate (40 g, 0.2 mol) in 100 ml of H<sub>2</sub>O was added to the impure **14** in 150 ml of methanol. The resulting copper chelate was extracted into hexane and evaporated of solvent, and the green solid remaining was crushed to a powder. Camphor was sublimed away from the chelate at  $100^\circ$  under vacuum (0.03 Torr). The ligand was freed from copper by washing an ether solution of the chelate with 10% H<sub>2</sub>SO<sub>4</sub>. When colorless, the ether layer was washed with aqueous NaHCO<sub>3</sub> solution, evaporated of solvent, and distilled. Isolated were 27.6 g (79%) of **14**, free of camphor according to nmr and glc analysis: bp  $82^\circ$  at 0.075 Torr. Tris[3-heptafluoropropylhydroxymethylene-*d*-camphorato]europium(III) (**15**) was then prepared.<sup>15, 41</sup>

**Nmr Spectra Using Shift Reagent.** Shift reagent **15** (286 mg) was dried under vacuum ( $100^\circ$ , 0.1 Torr) in a 3-in. test tube. To the septum capped tube was added 0.55 ml of dry carbon tetrachloride, 0.05 ml of TMS, and 0.30 mmol of dry sample. The test tube was centrifuged and the clear yellow supernatant solution syringed into a dry nitrogen filled nmr tube. This solution was 0.4 M in **15** and 0.5 M in sample. In recording spectra it was observed that variations in spinner speed in the MH-100 instrument caused the paramagnetic sample to induce field disrupting electrical currents in the shim coils. The problem was solved by constructing a spinner of high rotational moment of inertia.

**S-(+)-Benzyl- $\alpha$ -*d* Alcohol (S-(+)-**13**).** Benzaldehyde- $\alpha$ -*d* was prepared from benzaldehyde (40 g, 0.37 mol) by synthesizing the derivative  $\alpha$ -phenyl- $\alpha$ -morpholinacetone nitrile,<sup>42</sup> exchanging the active hydrogen with deuterium,<sup>43</sup> and generating benzaldehyde- $\alpha$ -*d* (30 g, 81% yield) by acid hydrolysis.<sup>42, 43</sup> The nmr spectrum showed approximately 96% monodeuteration had occurred. Benzaldehyde- $\alpha$ -*d* (24 g, 0.22 mol) was reduced in an actively fermenting dextrose and yeast (Red Star, Standard Brands, Inc.) solution.<sup>12</sup> Vacuum distillation gave 12.94 g (55%) of product. This was redistilled through a spinning band column to give 10.3 g of S-(+)-**13**, 100% pure by glc;  $[\alpha]^{25}_D +1.52 \pm 0.02$  ( $l = 1$ , neat). The deuterium content was evaluated mass spectrometrically at 11.5 eV. At this electron energy the M - 1 peak in benzyl alcohol was 0.46% of the parent ion peak. Five sweeps of the expanded benzyl alcohol spectrum were followed, under the same spectrometer conditions, by 5 sweeps of the benzyl- $\alpha$ -*d* alcohol spectrum. In calculating the isotope content, it was assumed that the M - 1 fragmentation peak was of the same intensity for both isotopically pure S-(+)-**13** and benzyl alcohol.<sup>44</sup> The average of two separate determinations gave  $94.3 \pm 0.7\%$  monodeuteration. The calculated optical rotation for 100% monodeuteration was  $[\alpha]^{25}_D +1.61 \pm 0.02$  or  $[\alpha]^{25}_D +1.54 \pm 0.03$  ( $l = 1$ , neat) (lit.<sup>12</sup>  $[\alpha]^{25}_D +1.58 \pm 0.01$  (neat)). The single benzyl proton magnetic resonance in the presence of chiral shift reagent showed only one enantiomer to be present (Figure 1).

**Alkoxysilanes.** Silylations of S-(+)-**13** were conducted using trialkylchlorosilanes with pyridine as acid acceptor.<sup>5</sup> Products were purified by distillation. Prepared from trimethylchlorosilane were 5.3 g of S-(+)-benzyl- $\alpha$ -*d*-oxytrimethylsilane (S-(+)-**5**),  $[\alpha]^{25}_D +1.66 \pm 0.06$  ( $c$  30.7, HCCl<sub>3</sub>), from triphenyldichlorosilane (mp  $95^\circ$ ) 6.6 g of S-(+)-benzyl- $\alpha$ -*d*-oxytriphenylsilane (S-(+)-**7**), mp  $82^\circ$  (lit.<sup>9</sup>  $83$ - $85^\circ$ ), and from trimethylchlorogermane 1.4 g of S-(+)-benzyl- $\alpha$ -*d*-oxytrimethylgermane.<sup>5</sup>

### Rearrangement of S-(+)-benzyl- $\alpha$ -*d*-oxytrimethylsilane (S-(+)-**5**).

(40) J. N. Eikenberry, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1972.

(41) K. J. Eisenbraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965).

(42) D. J. Bennett, G. W. Kirby, and V. A. Moss, *J. Chem. Soc. C*, 2049 (1970).

(43) D. Nasipuri and C. K. Ghosh, *J. Org. Chem.*, **35**, 657 (1970).

(44) It is possible that S-(+)-**13** might give a smaller M - 1 peak than benzyl alcohol, but this third-order isotope effect should be quite small. Its effect would be to make the measured isotope effect for metalation even larger.

(39) We thank Professor H. L. Goering for use of the polarimeter.

(a) **Derivatization with Acetic Acid.** *tert*-Butyllithium in pentane (29 ml, 36.5 mmol) was added to *S*-(+)-**5** (4.3 g, 23.5 mmol) in 30 ml of THF at  $-78^{\circ}$  and the mixture warmed slowly to  $-50^{\circ}$  to bring all the THF-*tert*-butyllithium complex into solution. Two mixtures after the addition of *tert*-butyllithium, excess glacial acetic acid in THF was injected at  $-78^{\circ}$ . Addition of water at  $0^{\circ}$ , followed by phase separation, solvent removal, and vacuum distillation, afforded an oil (4.2 g, 96%) consisting of 3 parts **13**, 24 parts recovered **5**, and 73 parts *S*-( $-$ )- $\alpha$ -hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -*d*-toluene (*S*-( $-$ )-**6**), 100% pure silylcarbinol by glc:  $[\alpha]^{25}_{\text{D}} -85.70 \pm 0.02$  ( $l = 1$ , neat);  $[\alpha]^{25}_{\text{D}} -90.5 \pm 0.03$  (*c* 5.0  $\text{HCCl}_3$ ). The nmr spectrum of **6** in the presence of chiral shift reagent showed four resonances at  $\delta$  2.99 (89.95%), 2.92 (2.25%), 2.88 (0.96%), and 2.83 (6.84%) in the trimethylsilyl region (Figure 3) showing that in addition to *S*-( $-$ )-**6** some of *R*-(+)-**6**, *S*-( $-$ )-**2**, and *R*-(+)-**2** were present. The assignments were made using the spectrum of a mixture of racemic **6** and racemic **2** (Figure 2). The deuterium content of the silylcarbinol was evaluated independently by nmr analysis without shift reagent present. A solution (65.45 mg) of 243.0 mg of benzyl alcohol in 7.77 g of acetonitrile was added to an nmr tube, followed by 80.35 mg of **6**, 0.2 ml of acetonitrile, 2 mg of pyridine, and 1 mg of  $\text{H}_2\text{SO}_4$  (to sharpen the OH resonance). Locked on the  $\text{SiMe}_3$  signal, the  $\text{PhCH}_2\text{OH}$  resonance at  $\tau$  5.49 and the benzyl proton resonance at  $\tau$  5.60 due to the minor component **2** in **6** were repeatedly swept in upfield and downfield directions at 100 MHz. The ratio of the intensity of the former to the latter peak was  $0.943 \pm 0.03$ . Neither resonance was saturated at the power level used. From this data it could be calculated that the rearrangement product contained  $9.21 \pm 0.45\%$  of the nondeuterated alcohol **2**. A second experiment gave the value  $9.64\%$  **2**, *av*  $9.42 \pm 0.45\%$ . Using the value  $5.67 \pm 0.68\%$  for the per cent of **1** in **5** (from the mass spectrum),  $k_{\text{H}}/k_{\text{D}} = 90.58 - (94.33 - 90.58) = 24 \pm 4$ . The per cent of **2** in **6** could not be determined accurately by mass spectrometry even at low voltage, due to interference from fragmentation.

(b) **Derivatization with Methyl Iodide.** *S*-(+)-**5** (1.0 g, 5.3 mmol) was metalated as described above. Anion solution (3 ml) was set aside at  $-196^{\circ}$  for later use *vide infra*. Methyl iodide (1 ml, 16.1 mmol) was added at  $-78^{\circ}$  to the remainder, and the solution was warmed to  $25^{\circ}$ . After 13 min the anion was recooled to  $-78^{\circ}$  and acetic acid in THF injected. Work-up gave an oil, consisting of two major compounds, which was separated by preparative glc. Isolated were 40 parts 1-phenyl-1-trimethylsilyloxyethane-1-*d* (**11**) and 60 parts **6**  $[\alpha]^{25}_{\text{D}} -37.0 \pm 0.02^{\circ}$  (*c* 13.4  $\text{HCCl}_3$ ). **11**:  $[\alpha]^{25}_{\text{D}} +0.65$  (*c* 3.1,  $\text{HCCl}_3$ ) (lit.<sup>45</sup>  $[\alpha]^{25}_{\text{D}} -45.5$  (*c* 4.91,  $\text{CH}_3\text{OH}$ ) for ( $-$ )-1-phenylethanol); nmr ( $\text{CCl}_4$ , TMS)  $\tau$  2.60 (m, 5, Ph), 8.54 (bs, 3,  $\text{CDCH}_3$ ), 9.88 (s, 9,  $\text{OSiMe}_3$ ). The remaining anion solution was also warmed to  $25^{\circ}$  for exactly 13 min but without methyl iodide present. Acid quench at  $-78^{\circ}$  gave upon work-up and purification by glc, **6**  $[\alpha]^{25}_{\text{D}} -80.8 \pm 0.02^{\circ}$  (*c* 6.9,  $\text{HCCl}_3$ ).

(45) R. Huisgen and C. Rüchardt, *Justus Liebig's Ann. Chem.*, **601**, 21 (1956).

**Brook Rearrangement of *S*-(1)- $\alpha$ -Hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -*d*-toluene *S*-( $-$ )-**6**.** A drop of sodium-potassium alloy (Na/K) was added to 0.4 g (2.2 mmol) of *S*-( $-$ )-**6**,  $[\alpha]^{25}_{\text{D}} -85.70 \pm 0.02^{\circ}$  ( $l = 1$ , neat), in 10 ml of dry ether at  $25^{\circ}$ . After 10 min, the ether solution was syringed away from the Na/K. Glc analysis showed 100% rearrangement to **5** had occurred. Cleavage by lithium aluminum hydride gave **13**,  $93 \pm 5\%$  monodeuterated by nmr. Nmr in the presence of chiral shift reagent showed 75% *S*-(+)-**13** and 25% *R*-( $-$ )-**13** to be present, showing 50% racemization and 50% inversion at carbon.

**Rearrangement of *S*-(+)-Benzyl- $\alpha$ -*d*-oxytriphenylsilane (*S*-(+)-**7**).** *tert*-Butyllithium (7.1 ml, 9.0 mmol) was added to *S*-(+)-**7** (3.0 g, 8.19 mmol) in 7 ml of THF. After 20 hr at  $-40^{\circ}$  acetic acid in THF was added at  $-78^{\circ}$ . Work-up gave, upon recrystallization from boiling heptane,  $\alpha$ -hydroxy- $\alpha$ -triphenylsilyl- $\alpha$ -*d*-toluene (**8**): mp  $114.2$  (lit.<sup>46</sup>  $116$ – $117^{\circ}$  for nondeuterated compound);  $[\alpha]^{25}_{\text{D}} -3.78 \pm 0.10^{\circ}$  (*c* 5.3  $\text{HCCl}_3$ ) (lit.<sup>23</sup>  $[\alpha]^{25}_{\text{D}} +49.5 \pm 1.1$  (*c* 1.77,  $\text{CHCl}_3$ ) for *R*-(+)-**4**). Careful nmr analysis showed  $89.39 \pm 0.96\%$  monodeuteration,  $k_{\text{H}}/k_{\text{D}} = 18 \pm 3$ . Nmr analysis in the presence of chiral shift reagent showed two resonances for the ortho-phenyl protons of the  $\text{SiPh}_3$  group at  $\delta$  10.7 and 11.80, ratio 54:45, and two resonances for the ortho-phenyl protons of the PhC group at  $\delta$  13.70 and 14.70, ratio 52:47, *av* ratio 53.4:46.6, or 93.2% racemization and 6.8% inversion. The optical rotation data indicated 92.4% racemization and 7.6% inversion to *S*-( $-$ )-**8** had occurred.

**Metalation of (*S*)-Benzyl- $\alpha$ -*d* Methyl Ether.** To *S*-(+)-benzyl- $\alpha$ -*d* alcohol (0.96 g, 8.8 mmol) in 6 ml of dry ether was added *n*-butyllithium (5.5 ml in hexane, 8.8 mmol) at  $-78^{\circ}$  and then dimethyl sulfate (1.1 g, 8.8 mmol). The temperature was raised to  $25^{\circ}$ . The benzyl methyl ether, formed in 80% yield, was purified by glc. To this ether (147 mg, 1.15 mmol), dissolved in 1 ml of THF at  $-78^{\circ}$ , was added *tert*-butyllithium (1 ml in pentane, 1.26 mmol) and after 85 sec at  $-78^{\circ}$  methyl iodide (0.4 g, 28 mmol). A white precipitate formed immediately. Work-up gave racemic 1-phenylethyl-1-*d* methyl ether, containing a minor amount of its undeuterated isomer: nmr ( $\text{CCl}_4$ , TMS)  $\tau$  2.71 (s, 5, Ph), 6.82 (s, 3,  $\text{OCH}_3$ ), 8.61 (t, 3,  $\text{CDCH}_3$ ,  $J_{\text{H-D}} = 0.9$  Hz). A careful comparison of the intensities of the residual proton resonance at  $\tau$  5.80 with that in 1-phenylethyl methyl ether gives the value  $9.35 \pm 0.55$  for the per cent monodeuteration,  $k_{\text{H}}/k_{\text{D}} = 25 \pm 5$ .

**Rearrangement of *S*-(+)-Benzyl- $\alpha$ -*d*-oxytrimethylgermane (*S*-(+)-**15**).** To *S*-(+)-**15** (1.4 g, 6.2 mmol) in 10 ml of THF was added *tert*-butyllithium (10 ml in pentane, 12.4 mmol). After 3 min at  $-50^{\circ}$ , acetic acid in THF was added at  $-78^{\circ}$ . Work-up gave 80% *S*-(+)- $\alpha$ -hydroxy- $\alpha$ -trimethylgermyl- $\beta$ -*d*-toluene (**16**), 100% pure:  $[\alpha]^{25}_{\text{D}} -82.1$  (*c* 12.6  $\text{HCCl}_3$ ). Nmr analysis in the presence of chiral shift reagent gave four resonances in the trimethylgermyl region which were integrated:  $\delta$  3.04 (89.5%), 2.99 (2.54%), 2.88 (1.78%), 2.84 (5.53%).

(46) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Amer. Chem. Soc.*, **81**, 981 (1959).