Oxiranyl Anions. Improved Synthesis of Trimethylsilyl-Substituted Oxiranyl Anions and Their Addition to Aldehydes and Ketones

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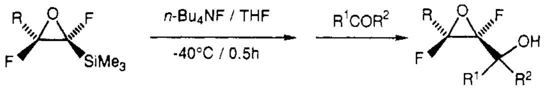
Conditions for the metalation of trimethylsilyl-substituted oxiranes have been optimized. Utilizing *sec*-butyllithium in diethyl ether with tetramethylethylenediamine, oxiranyl anions possessing virtually all substitution patterns are generated in excellent yields. These unique carbanions are stable to α-elimination for periods of hours at −116 °C. Most of the anions exhibit strict retention of configuration at the metalated carbon stereocenter, although one example displaying configurational inversion has been discovered. Reactions with aldehydes and ketones have been explored. Although low diastereoselectivity in reactions with alkyl aldehydes is observed, good to excellent diastereofacial addition to ketone and conjugated aldehydes can be achieved.

Oxiranes are widely recognized as extremely versatile synthetic intermediates.[2] The enhanced reactivity of these species, attributable to a high degree of ring strain, permits a range of nucleophilic ring openings, Lewis acid catalyzed rearrangements, and isomerization reactions. The ready accessibility of oxiranes further contributes to their usefulness. Epoxidation of olefins utilizing a variety of general reaction conditions (depending on whether the olefin is nucleophilic or electrophilic) permits the generation of oxiranes with substantial stereochemical control. Oxiranes can be generated in high enantiomeric excesses by direct oxidation of allylic alcohols.[3] Cyclization of halohydrins and methods based upon ylide chemistry[4] nicely complement the direct oxidation of olefins for the synthesis of oxiranes. In view of its many roles in organic synthesis, unique methods for the introduction of the epoxide functional group into organic molecules would appear to be highly valued.

One method for the incorporation of oxiranes that has yet to be fully developed is the reaction of oxiranyl anions with reactive electrophiles. Oxiranyl anion intermediates were first proposed by House in 1958 in conjunction with his studies on base-catalyzed isomerizations of oxiranes.[5] These anions were examined further in the same context by Cope[6] and Crandall.[7] Since that time, numerous reports implicating metalated oxirane intermediates have been recorded.[8] According to these studies, unstabilized oxiranyl anions are especially prone to α-elimination, providing α-alkoxy carbenes. Products derived from α-alkoxy carbenes have been detected in numerous instances in which oxiranes are subjected to strongly basic conditions.

Other methods besides metal–hydrogen exchange provide potential entries to oxiranyl anions or their synthetic equivalents. For example, desilylation of epoxysilanes with fluoride, first investigated by Chan and co-workers, ostensibly involves transient oxiranyl anions or hypervalent silicon "ate" complexes.[9] The fact that desilylation occurs with strict retention of configuration prior to α-elimination indicates that the nucleophilic species has a finite lifetime. This desilylation reaction has been used in synthetic sequences leading to natural products[10] and as a means of generating allene oxides.[11] Fluorinated oxiranyl anions have also been produced by the desilylation reaction, and these nucleophiles undergo 1,2-carbonyl addition reactions with a variety of aldehydes and ketones (eq 1).[12]



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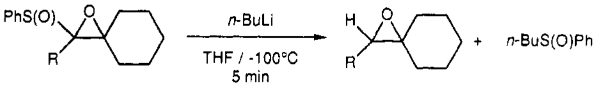
Oxiranyl anions also appear to be generated as fleeting intermediates in the desulfinylation of epoxy sulfoxides.[13] Treatment of the latter with n-butyllithium leads to the unsubstituted epoxides, presumably through a transient oxiranyl anion (eq 2).



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Eisch and Galle were the first to conduct a thorough study of the generation and nucleophilic reactions of functionalized oxiranyl anions.[14] Their pioneering research demonstrated the apparent necessity of an anion-stabilizing group to enhance the facility of metalation of epoxides and to increase the stability of the oxiranyl anions produced. Deprotonation of cis-disubstituted oxiranes and subsequent reaction of the resultant oxiranyl anions with simple electrophiles, such as Me_3SiCl, Me_3SnCl, CO_2, MeI, amides, and D_2O, led to high yields of the desired products. Conversely, the reactivity of trans-disubstituted substrates toward strong bases proved to be much lower, and only moderate yields of substituted epoxides were obtained (eq

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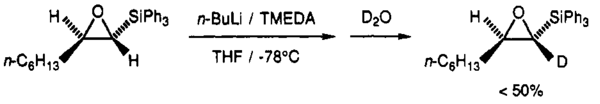
3). In both cases complete configurational stability was observed.



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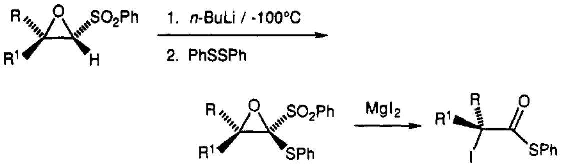
In related studies, Jackson and coworkers reported the preparation of a phenylsulfonyl-substituted oxiranyl anion and its application as an acetaldehyde dipolar synthon (eq 4).[15]

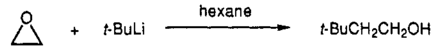


(4)

In view of the potential of metalated oxiranes to enhance and expand methods for the construction of epoxides, we have initiated investigations on the application of these unique nucleophiles in organic synthesis. Herein we describe our initial efforts in this area, outlining an improved synthesis of trimethylsilyl-substituted oxiranyl anions and the reaction of these nucleophiles with a variety of aldehyde and ketone electrophiles.

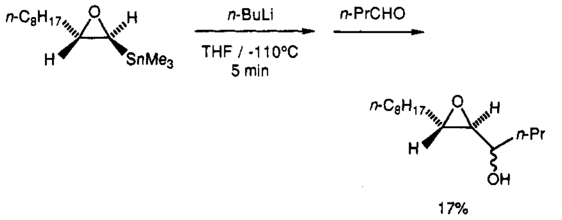
Results and Discussion

At the outset of our studies, we had hoped to develop routes to nonstabilized oxiranyl anions. However, several attempts to metalate simple unfunctionalized oxiranes were unsuccessful. Subjection of ethylene oxide to an assortment of metalating conditions failed to provide any evidence for generation of the desired oxiranyl anion. Similar observations were made by Eisch, who reported that ethylene oxide provided the product resulting from nucleophilic ring opening of the epoxide in reactions with *tert*-butyllithium (eq 5).[14b,d]



(5)

An alternative route to unfunctionalized oxiranyl anions was also briefly explored. A trimethylstannyl-substituted oxirane was synthesized in order to test the feasibility of tin–lithium exchange for the generation of oxiranyl anions. Treatment of the trimethylstannyl oxirane with *n*-butyllithium, followed by a quench with butanal after 5 min, afforded only 17% of the desired carbonyl addition product (eq 6). Longer reaction times before the quench led to complete decomposition, and with shorter reaction times the metalation was not complete. During the course of this investigation, Eisch reported similar results in attempts to generate oxiranyllithium species by transmetalation from oxiranylstannanes.[14d]



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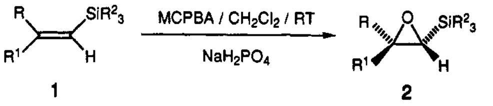
The apparent requirement for an anion-stabilizing substituent led us to investigate trimethylsilyl-substituted oxiranyl anions and the reaction of these nucleophiles with aldehydes and ketones. Most of the desired epoxysilanes were prepared by epoxidation of the appropriate alkenylsilanes with *m*-chloroperbenzoic acid using Na_2HPO_4 as a buffer (eq 7, Table I).[16] Stereodefined alkenylsilane precursors for the epoxidation reactions were readily available by utilizing a variety of published procedures.[17] *cis*-Epoxysilanes show greater coupling constants (4–5 Hz) than the corresponding trans-disubstituted isomers (3–4 Hz), making ^1H NMR a convenient method for distinguishing between the two isomers.[18] The preparation of the trisubstituted epoxysilane **2g** is described in the literature (eq 8).[19]

Table I. Preparation of Trimethylsilyl-Substituted Oxiranes

starting material	R	R^1	R^2	% isolated yield (2)
1a	n-C$_8$H$_{17}$	H	Me	88
1b	t-Bu	H	Me	63
1c	H	n-C$_8$H$_{17}$	Me	80
1d	H	n-C$_7$H$_{15}$	Me	71
1e	H	t-Bu	Me	56
1f	n-C$_8$H$_{17}$	H	Ph	71



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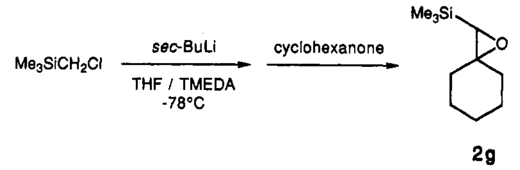

(8)

Once in hand, the trimethylsilyl-substituted oxiranes were subjected to a variety of metalation conditions in order to optimize the generation of oxiranyl anions. Butanal was chosen as a standard electrophile for trapping these anions (eq 9). Utilization of *sec*-butyllithium (1.2 equiv) as base with tetramethylethylenediamine (TMEDA, 1.2 equiv) in diethyl ether at −116 °C proved to be the most efficient protocol for all substitution patterns of trimethylsilyl oxiranes (Table II). Under these conditions cis-disubstituted epoxysilanes were easily deprotonated within 10 min, and the resulting anions were trapped by butanal in good yields to provide two diastereomeric products (entries 1 and 5). The deprotonation of trans-disubstituted and trisubstituted epoxysilanes was a much slower process, requiring 3–4 h for complete reaction (en-

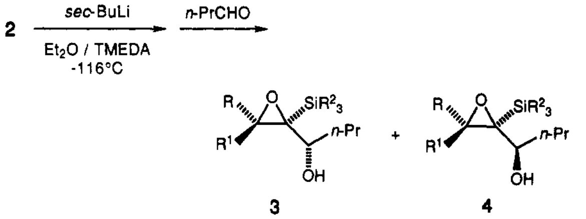

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Table II. Metalation of Epoxysilanes and Reaction with Butanal

entry	starting material	reaction time	% isolated yield (3 + 4)	diastereomeric ratio (3:4)
1	**2a**	10 min	83	2:1
2	**2c**	4 h	63	1:1.3
3	**2d**	4 h	73	1:2
4	**2e**	–	0	–
5	**2f**	10 min	82[a]	1.3:1
6	**2g**	3 h	56	2.4:1

[a] After desilylation with *n*-Bu$_4$NF in DMSO.

tries 2, 3, and 6). Nevertheless, the desired epoxy alcohols could again be isolated in good yields with moderate diastereoselectivity. These results indicate that trimethylsilyl-substituted oxiranyl anions are stable for periods of hours at −116 °C in ether solvent and can subsequently be trapped by carbonyl electrophiles to provide reasonable yields of the desired products. Among the silylepoxides examined, only *trans*-1-(trimethylsilyl)-1,2-epoxy-3,3-dimethylbutane (**2e**) failed to undergo metalation (entry 4). The diastereoselectivity for the various oxiranyl anion substitution patterns was disappointingly low, but in line with the stereochemistry observed in the reaction between (2,2-dimethylcyclopropyl)magnesium bromide and acetaldehyde.[20] It is interesting to note that the size of substituents on silicon had a minimal effect on the observed diastereoselectivity (compare entries 1 and 5).

Although steric hindrance in the approach of the base to the C–H bond has been suggested as one explanation for the differential reactivity between cis-disubstituted epoxysilanes and the oxiranes possessing other substitution patterns, at least one other factor must be considered as well. As in the base-promoted isomerization of epoxides, metalation may take place from a base–epoxide complex.[8] Ignoring any aggregation phenomena, two such complexes exist (eq 10). The existence and stabilities of these complexes will be determined largely by steric interactions between the base and the substituents on the oxirane. Cis-disubstituted oxiranes will favor a complex placing the base syn to the acidic proton, and the equilibrium constant for formation of a complex is expected to be high. The equilibrium constant for formation of an organolithium–epoxide complex in trans-disubstituted oxiranes and trisubstituted substrates will be somewhat lower and more equally split between the two complexes. The rate of deprotonation of oxiranes possessing these substitution patterns is therefore expected to be dramatically lower.

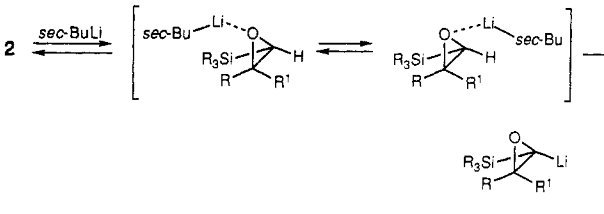

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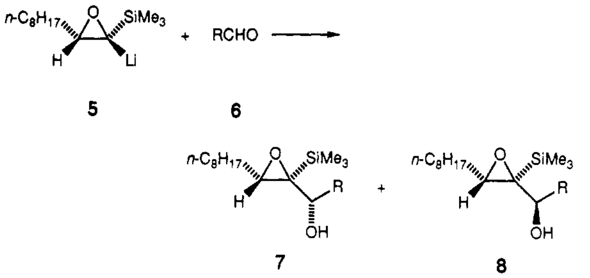
Table III. Diastereoselectivity in Reaction of Aldehydes (6) with Oxiranyl Anion 5

entry	aldehyde	R	% isolated yield (7 + 8)	diastereomeric ratio (7:8)[a]
1	**6a**	*i*-Pr	73	2.4:1
2	**6b**	*t*-Bu	83	2:1
3	**6c**	Ph	73	7.7:1
4	**6d**	*trans*-MeCH=CH	72	4:1
5	**6e**	PhC≡C	45	2.5:1
6	**6f**	MeCH(Ph)	66	–[b]

[a] Tentative stereochemical assignments have been made based on spectral correlations. [b] A mixture of four diastereomers in the ratio of 2:2:1:1 was generated.

Because the oxiranyl anions all showed nearly the same diastereoselectivity in the reaction with butanal, the oxiranyl anion derived from epoxysilane **2a** was chosen as a model to study the effects of various aldehyde substituents on diastereoselectivity in 1,2-addition reactions (eq 11, Table III). Surprisingly, increasing the steric demands of the aldehyde had little influence on the diastereomeric ratio of the observed products (compare entry 1, Table II, with entries 1 and 2, Table III). α,β-Unsaturated aldehydes provided only products of 1,2-addition, and in general higher diastereoselectivities were observed with these substrates than for simple alkyl aldehydes (entries 3 and 4, Table III).



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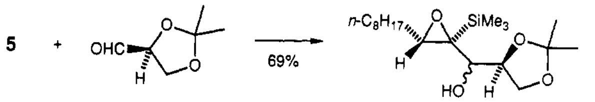
Heterosubstituents α to the carbonyl were not influential in enhancing diastereoselectivity. Thus, (4*S*)-2,2-dimethyl-4-formyl-1,3-dioxolane provided an equal mixture of four diastereomers upon treatment with oxiranyl anion **5** (eq 12).



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(1 : 1 : 1 : 1 mixture of diastereomers)

In order to assess the influence of TMEDA on the diastereoselectivity of the process, an experiment was devised to generate the oxiranyl anion in the absence of this additive. Thus, the oxiranyl anion derived from **2a** was trapped by trimethyltin bromide, and the resultant oxiranylstannane was isolated in 85% yield (eq 13). Transmetalation with *n*-butyllithium[21] followed by addition of butanal provided a mixture of **3a** and **4a** in ratios of from 3 to 5:1. Although the absence of TMEDA allows somewhat higher diastereoselectivities to be achieved, the extra effort required to accomplish these transformations detracts from this protocol.

Seebach and co-workers reported that diastereoselectivity in the addition of aziridinyllithium anions to aldehydes could be dramatically improved by transmetalation using ClTi(NEt$_2$)$_3$.[22] In an effort to increase

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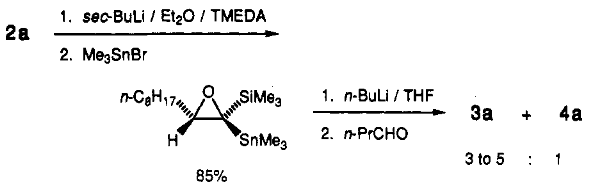

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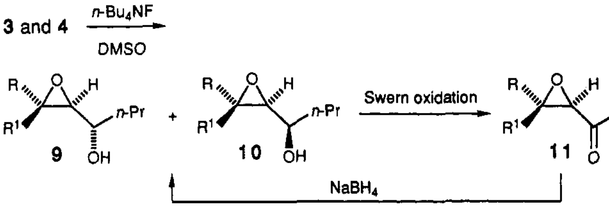
diastereoselectivity in carbonyl addition reactions of oxiranyl anions, transmetalation to more highly selective organometallics was attempted. Only weakly Lewis acidic transmetalating agents seemed appropriate possibilities, because strong Lewis acids presented the danger of facilitating epoxide ring-opening and therefore lowering the yield of the desired products. In the present case, transmetalation with magnesium bromide, cerium trichloride, cerium triiodide, and $ClTi(NEt_2)_3$ provided reasonable yields of carbonyl addition product (43–84%) in reactions of **5** with butanal, but diastereoselectivity in these reactions remained about 2:1. In this brief survey, $ClTi(O\text{-}i\text{-}Pr)_3$ showed the most promise as a transmetalating agent in terms of diastereoselectivity (providing an 8:1 mixture of diastereomers in reaction of **5** with butanal), but yields of the desired products were low (40%). Work continues in this area to determine if useful transmetalation/carbonyl addition procedures can be developed.

The relative stereochemistry of the carbonyl addition products was assigned utilizing several different techniques. For two substrates, the assignment of stereochemistry was made by direct comparison to compounds prepared by an unambiguous route. The reduction of α,β-epoxy ketones with sodium borohydride proceeds with high diastereoselectivity to form the corresponding α,β-epoxy alcohols of known relative configuration.[23] Based on this precedent, it was possible to assign the relative stereochemistry of diastereomers **3a** and **4a** (eq 14).



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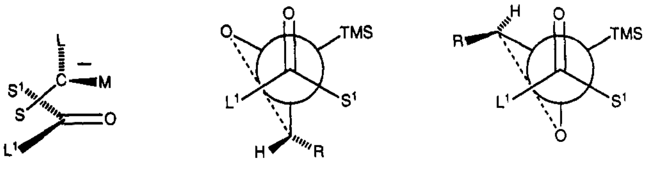
Stereospecific desilylation of **3a** and **4a** provided epoxy alcohols **9a** and **10a**. Swern oxidation afforded epoxy ketones **11a**, which could be reduced with $NaBH_4$ to provide an 84:16 mixture of alcohols **9a** and **10a**, respectively. These epoxy alcohols could be compared to the epoxy alcohols prepared by the desilylation reactions in order to make the stereochemical assignment. The major diastereomer obtained by addition of the oxiranyl anion derived from **3a** to butanal is the same as the major diastereomer obtained by $NaBH_4$ reduction of **11a**. Thus the relative stereochemistry of the major diastereomer formed by oxiranyl anion addition to butanal in the cis-disubstituted epoxide series was assigned as (R^*,S^*)-**3a**. In the same fashion, the reduction of **11d** (R = H, $R^1 = n\text{-}C_7H_{15}$) with $NaBH_4$ provided a 92:8 mixture of the corresponding alcohols **9d** and **10d**. The minor diastereomer from this reaction matched in every respect with the major diastereomer from the corresponding oxiranyl anion carbonyl addition product, and thus **4d** possesses the R^*,R^* relative stereochemistry. It should be pointed out that the same sense of relative asymmetric induction as displayed in Table III can be achieved when appropriate trimethylsilyl-substituted allylic alcohols are epoxidized with *m*-chloroperbenzoic acid or $VO(acac)_2/t\text{-}BuOOH$.[24] Alternatively, treatment of trimethylsilyl-substituted epoxy aldehydes with organolithium or Grignard reagents also provides entry to the major diastereomers provided by oxiranyl anion addition to aldehydes.[25]



12 **13**

Figure 1. Empirical transition structure models for addition of oxiranyl anions to prochiral aldehydes and ketones.

The relative stereochemistry of products in Table III was assigned by correlation with the butanal carbonyl addition products. Without exception, the major isomer proved to be the less polar one (as determined on the basis of TLC and GLC behavior), and the carbinol proton of this diastereomer appeared at lower field in the ^1H NMR spectrum compared to that of the minor isomer. The ^{13}C NMR spectrum was equally informative. In each set of diastereomers, carbons attached to oxygen appeared at higher field in the major diastereomer when compared to those of the minor diastereomer.

The relative stereochemistry of the major diastereomeric epoxy alcohol derived from **2g** and butanal (entry 6, Table II) was established by single-crystal X-ray diffractometry.

Clearly, energy differences are extremely small between the two diastereomeric transition states leading to product in these examples. However, for those products for which unambiguous stereochemical assignments have been made, it is interesting to note that by and large the reactions conform to the simple (empirical) steric model for reaction of chiral anions with aldehydes introduced by Bassindale and Taylor (Figure 1).[26] For all substitution patterns of the oxiranyl anions, the trialkylsilyl group must be considered the largest substituent. In the case of cis-disubstituted oxiranyl anions, the oxygen of the oxirane could be considered the medium-sized substituent (**12**), but for trans-disubstituted oxiranes the oxygen might be considered the small group (**13**). This reversal can be rationalized by noting that the alkyl substituent β to the silicon will be directed either toward the incoming electrophile or away from the incoming electrophile depending on the stereochemistry about the epoxide. The net result is that the reaction of cis-disubstituted oxiranyl anions with aldehydes provides products possessing the opposite relative stereochemistry as those of the trans-disubstituted series. The sense of relative asymmetric induction elicited by the single trisubstituted oxiranyl anion utilized would be anomalous by this model. The fact that the β-substituents are constrained to a ring in this case creates still further questions concerning the steric priorities of the various substituents, and thus no clear-cut conclusions can be reached in this case. Because energy difference are so small, and because the model does not address the role of the counterion nor any aggregation phenomena that may be present, a definitive model awaits more detailed studies.

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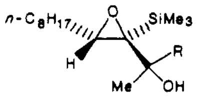
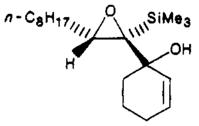
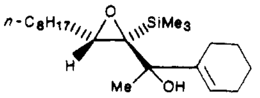
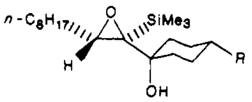
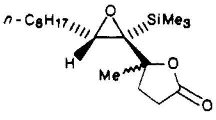
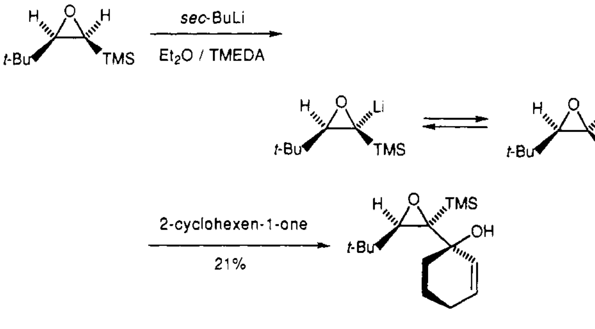
Table IV. Reaction of Oxiranyl Anion 5 with Various Aldehydes and Ketones

entry	substrate	product	% isolated yield	diastereoselectivity
1	acetophenone	 R = Ph (14)	81	9:1
2	pinacolone	R = t-Bu (15)	56	>200:1
3	2-cyclohexen-1-one	 (16)	79	7.7:1
4	1-acetyl-1-cyclohexene	 (17)	60	2.5:1
5	4-*tert*-butylcyclohexanone	 R = t-Bu (18)	76	>20:1
6	4-methylcyclohexanone	R = Me (19)	81	1.5:1
7	ethyl levulinate	 (20)	48	1.5:1

Five acyclic ketones were utilized in reactions with oxiranyl anion **5**, demonstrating that good to excellent diastereoselectivity could be achieved in the addition of oxiranyl anions to carbonyl substrates (Table IV, entries 1, 2, 4, and 7). No convenient, unambiguous means of determining the relative configuration of these species was found, and so any assignments made are tentative. It was initially surprising to find that ketones and conjugated (stabilized) aldehydes provided generally higher diastereomeric ratios of products than simple alkyl aldehydes. These results may be interpreted in terms of an early transition state reaction. With more reactive aldehydes, carbon–carbon bond formation is established at an early point on the reaction coordinate, and steric demands of the aldehyde substituents are apparently not highly influential. As a consequence, diastereoselectivity is relatively poor. In the case of less reactive aldehydes and ketones, the commitment to carbon–carbon bond formation is established further along the reaction coordinate, permitting steric effects to play a greater role in the determination of the transition state structure. Higher observed diastereoselectivities therefore result.

Three cyclic ketones were also examined in this study. Within the limits of detection, 2-cyclohexen-1-one undergoes exclusive 1,2-carbonyl addition with good diastereoselectivity (Table IV, entry 3). 4-*tert*-Butylcyclohexanone provides a single diastereomeric product (Table IV, entry 5), presumably resulting from equatorial attack of the oxiranyl anion, but 4-methylcyclohexanone (entry 6) affords a 1.5:1 mixture of diastereomeric products in good yield.

In all of the examples cited thus far, complete configurational stability of the oxiranyl anion has been observed. In fact, previous reports of trimethylsilyl-substituted oxiranyl anions indicated that isomerization had not been observed in any substrates studied under conditions where the oxiranyl anions are stable to α-elimination.[14] During the course of our study, we encountered one example in which configurational inversion appears to be a relatively facile process. When *cis*-1-(trimethylsilyl)-1,2-epoxy-3,3-dimethylbutane was metalated under the standard reaction conditions and then treated with 2-cyclohexen-1-one, the major product was a solid, which was isolated in 21% yield (eq 15). Single-crystal X-ray analysis of this product showed that isomerization of the oxiranyl anion had occurred prior to carbonyl addition. Presumably, the strain created in forcing the *tert*-butyl group and the trimethylsilyl group cis on the oxirane ring facilitates the isomerization process. Unfortunately, no inversion barriers of oxiranyl anions have yet been established. Calculations of cyclopropyl anions show reduced inversion barriers for anions bearing inductively stabilizing substituents (e.g., CF_3, 94 kJ mol^{-1}) and for mesomeric stabilizing groups attached to the anionic center (e.g., CN, 39 kJ mol^{-1}) when compared to the cyclopropyl anion itself (136 kJ mol^{-1}).[27] As far as we are aware, no studies concerning the influence of substituents on the heat of formation of oxiranes have been conducted, although it has been reported that the interaction of methyl groups in 2,2,3-trimethylthiacyclopropane causes the heat of formation to be 71 kJ mol^{-1} more positive than expected without steric corrections.[28] Consequently, considerable strain is anticipated in the sterically bulky oxiranyl anions, and this strain can be relieved to a substantial degree by an epimerization



(15)

(21)

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[27] Wagner, H.-U.; Boche, G. *Z. Naturforsch B* **1982**, *37b*, 1339.

[28] Pihlaha, K.; Taskinen, E. *Physical Methods in Heterocyclic Chemistry*; Academic Press: New York, 1974; Vol. IV, p 199.

process. Certainly further studies into this phenomena are warranted.

Conclusions

An improved synthesis of trimethylsilyl-substituted oxiranyl anions has been described. Use of *sec*-butyllithium in Et_2O with TMEDA permits efficient metalation of epoxysilanes under exceedingly mild conditions. Virtually all substitution patterns of the desired oxiranyl anions can be accessed in good yields. These unique organolithiums have appreciable stability for periods of hours at very low temperatures, although one intermediate displaying facile configurational inversion has been discovered.

Reactions of these chiral nucleophiles with an assortment of aldehydes and ketones have been examined. Whereas diastereoselectivities for simple alkyl aldehydes are low, modest to excellent diastereoselectivities can be achieved with ketones and α,β-unsaturated aldehydes. Transmetalation to oxiranyltitanium species shows promise in increasing diastereoselectivity, and work in this area continues.

Oxiranyl anions present many interesting and unique opportunities for further exploration and represent promising nucleophilic species for stereoselective organic synthesis. In subsequent studies, we hope to exploit further the enormous potential of these intermediates as useful synthons for organic synthesis.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were recorded on an FT-IR spectrophotometer. ^1H NMR spectra were recorded at 90, 250, or 300 MHz, with $CDCl_3$ both as solvent and internal standard ($\delta = 7.24$ ppm). ^{13}C NMR spectra were recorded at 23, 63, or 75 MHz, with $CDCl_3$ both as solvent and internal standard ($\delta = 77.00$ ppm). Capillary gas–liquid chromatographic analyses were performed using 25 m SE-54 or 30 m Carbowax DX-3 fused silica capillary columns. Flash chromatography was carried out by using standard procedures.[29] Diethyl ether and THF were distilled from sodium benzophenone ketyl under argon immediately prior to use. All reactions were conducted under a positive pressure of argon, utilizing standard bench-top techniques for handling of air-sensitive materials.[30] All title compounds were judged to be >95% pure by ^1H NMR and ^{13}C NMR spectral determinations.

General Procedure for the Preparation of (*Z*)-1-(Trialkylsilyl)-1-alkenes. DIBAL-H (0.5 mL, 2.75 mmol) was added to a solution of 2.52 mmol of 1-(trialkylsilyl)-1-alkyne in 4 mL of Et_2O at room temperature. The reaction was then heated at reflux for 4 h. After cooling to 0 °C the reaction mixture was cautiously treated with 3 N NaOH (30 mL), extracted with hexanes (3×), washed with 3 N NaOH and brine, dried, concentrated, and distilled.

(*Z*)-1-(Triphenylsilyl)-1-decene (1f). By use of the general procedure above, **1f** was prepared from 1-(triphenylsilyl)-1-decyne in 92% yield. ^1H NMR: δ 7.64–7.28 (m, 15 H), 6.69 (m, 1 H), 6.02 (d, $J = 14.0$ Hz, 1 H), 1.90 (m, 2 H), 1.26 (m, 12 H), 0.86 (m, 3 H). IR: 3080, 1610 cm^{-1}.

General Procedure for Epoxidation of Alkenylsilanes. A solution of *m*-chloroperbenzoic acid (85%, 6.64 g, 38.5 mmol) in 65 mL of CH_2Cl_2 was added at room temperature to a mixture containing 28.3 mmol of alkenylsilane and anhydrous Na_2HPO_4 (6.21 g, 43.7 mmol) in 60 mL of CH_2Cl_2. The mixture was stirred until GLC analysis showed complete reaction (12–22 h). Saturated $NaHSO_3$ solution (20 mL) was added, and the mixture was stirred for 30 min. Saturated $NaHCO_3$ solution (80 mL) was next added carefully, and stirring was continued for another 30 min. The organic layer was separated, washed with saturated $NaHSO_3$ solution and brine, dried, and concentrated, and the crude epoxide was distilled.

***cis*-1-(Trimethylsilyl)-1,2-epoxydecane (2a).** By use of the general procedure, **2a** was prepared from (*Z*)-1-(trimethylsilyl)-1-decene (**1a**) in 88% yield, bp 60 °C (0.01 mmHg). ^1H NMR: δ 3.06 (m, 1 H), 2.16 (d, $J = 5.2$ Hz, 1 H), 1.58–1.25 (m, 14 H), 0.85 (m, 3 H), 0.10 (s, 9 H). ^{13}C NMR: δ 57.56, 50.49, 31.73, 31.50, 29.42, 29.08, 26.95, 22.51, 13.88, –1.88. IR: 2920, 850 cm^{-1}. Exact mass calcd for $C_{13}H_{28}OSi$ (M^+) 228.1909, found 228.1887.

***cis*-1-(Trimethylsilyl)-1,2-epoxy-3,3-dimethylbutane (2b).** By use of the general procedure, **2b** was prepared from (*Z*)-1-(trimethylsilyl)-3,3-dimethyl-1-butene (**1b**) in 63% yield after Kugelrohr distillation, bp 70 °C (15 mmHg). ^1H NMR: δ 2.89 (d, $J = 5.3$ Hz, 1 H), 2.14 (d, $J = 5.3$ Hz, 1 H), 0.92 (s, 9 H), 0.17 (s, 9 H). ^{13}C NMR: δ 67.41, 51.21, 31.52, 26.75, –0.46. IR: 2980, 860 cm^{-1}. Exact mass calcd for $C_9H_{20}OSi$ (M^+) 172.1283, found 172.1280.

***trans*-1-(Trimethylsilyl)-1,2-epoxydecane (2c).** *n*-Butyllithium (55 mL, 88.0 mmol, 1.6 M in hexanes) was added dropwise to a mixture of potassium *tert*-butoxide (9.85 g, 87.5 mmol) in 44 mL of hexanes at 0 °C. The mixture was warmed to room temperature, stirred for 30 min, cooled to –78 °C, and treated with allyltrimethylsilane (10.0 g, 87.5 mmol). Stirring was continued for 4 h while the mixture was allowed to warm to room temperature. After cooling to –78 °C again, 1-bromoheptane (9.16 mL, 58.3 mmol) in 30 mL of Et_2O was slowly added, and the resulting mixture was stirred overnight while warming to room temperature. After washing with water and brine, the organic layer was dried and concentrated. Direct epoxidation of the resulting crude oil with the general procedure above afforded 11.2 g (49.0 mmol, 84%) of **2c**, bp 70 °C (0.02 mmHg). ^1H NMR: δ 2.73 (m, 1 H), 1.94 (d, $J = 3.5$ Hz, 1 H), 1.60–1.25 (m, 14 H), 0.85 (m, 3 H), 0.03 (s, 9 H). ^{13}C NMR: δ 56.14, 51.67, 34.07, 31.85, 29.46, 29.22, 26.35, 22.64, 14.05, –3.66. IR: 2930, 840 cm^{-1}. Exact mass calcd for $C_{13}H_{28}OSi$ (M^+) 228.1909, found 228.1916.

***trans*-1-(Trimethylsilyl)-1,2-epoxynonane (2d).** Use of the procedure given for **2c** (alkylation with 1-bromohexane in place of 1-bromoheptane) afforded **2d** in 71% yield, bp 60 °C (0.02 mmHg). ^1H NMR: δ 2.73 (m, 1 H), 1.93 (d, $J = 3.5$ Hz, 1 H), 1.62–1.25 (m, 12 H), 0.85 (m, 3 H), 0.03 (s, 9 H). ^{13}C NMR: δ 56.07, 51.56, 34.03, 31.73, 29.39, 29.20, 26.30, 22.56, 13.97, –3.74. IR: 2975, 840 cm^{-1}. Exact mass calcd for $C_{11}H_{23}OSi$ (M – 15) 199.1519, found 199.1549.

***trans*-1-(Trimethylsilyl)-1,2-epoxy-3,3-dimethylbutane (2e).** By use of the general epoxidation procedure, **2e** was prepared from (*E*)-1-(trimethylsilyl)-3,3-dimethyl-1-butene (**1e**) in 56% yield after Kugelrohr distillation, bp 130 °C. ^1H NMR: δ 2.87 (d, $J = 3.6$ Hz, 1 H), 2.41 (d, $J = 3.6$ Hz, 1 H), 1.21 (s, 9 H), 0.35 (s, 9 H). ^{13}C NMR: δ 63.98, 47.39, 30.89, 25.42, –4.01. IR: 2975, 850 cm^{-1}. Exact mass calcd for $C_8H_{17}OSi$ (M – 15) 157.1049, found 157.1066.

***cis*-1-(Triphenylsilyl)-1,2-epoxydecane (2f).** By use of the general epoxidation procedure, **2f** was prepared from (*Z*)-1-(triphenylsilyl)-1-decene (**1f**) in 71% yield after flash chromatography (silica gel, 20:1 hexanes–EtOAc); colorless solid, mp 65 °C. ^1H NMR: δ 7.65–7.34 (m, 15 H), 3.31 (m, 1 H), 3.01 (d, $J = 5.0$ Hz, 1 H), 1.33–1.04 (m, 14 H), 0.88 (m, 3 H). ^{13}C NMR: δ 135.86, 133.26, 129.79, 127.84, 58.07, 48.47, 31.68, 30.49, 29.03, 26.70, 22.56, 14.03. IR: 3070, 2965 cm^{-1}. Exact mass calcd for $C_{28}H_{34}OSi$ (M^+) 414.2379, found 414.2364.

General Procedure for the Metalation of Epoxysilanes and Reaction with Electrophiles. A solution of the epoxysilane (1.24 mmol) and TMEDA (0.22 mL, 1.49 mmol) in 30 mL of Et_2O at –116 °C was treated with *s*-BuLi (1.14 mL, 1.49 mmol, 1.3 M in cyclohexane). The resulting yellow solution was stirred at –116 °C until metalation was complete. The electrophile (1.62 mmol) was dissolved in 10 mL of Et_2O, and the solution was cooled to –116 °C and then added to the oxiranyl anion solution. After warming to room temperature the mixture was poured into 10 mL of saturated NH_4Cl solution. The organic layer was separated, washed with brine, dried over anhydrous $MgSO_4$, and concentrated.

Metalation of 2a and Reaction with Butanal. By use of the general procedure, **2a** (377 mg, 1.65 mmol) was metalated and subsequently treated with butanal to afford **(4*R**,5*S**,6*R**)-5,6-epoxy-5-(trimethylsilyl)tetradecan-4-ol (3a)** (274 mg, 0.898

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[29] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[30] Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975.

mmol, 53%) and **(4R*,5R*,6S*)-5,6-epoxy-5-(trimethylsilyl)tetradecan-4-ol (4a)** (152 mg, 0.506 mmol, 30%) after flash chromatography on silica gel (20:1 hexanes–EtOAc).

3a. ^{1}H NMR: δ 3.83 (m, 1 H), 3.05 (m, 1 H), 2.18 (s, 1 H), 1.50–1.25 (m, 18 H), 0.95–0.83 (2 m, 6 H), 0.13 (s, 9 H). ^{13}C NMR: δ 68.70, 57.52, 35.80, 31.65, 29.92, 29.03, 28.77, 26.79, 22.58, 18.55, 14.08, −1.38. IR: 3490 cm^{-1}. Exact mass calcd for $C_{17}H_{35}O_2Si$ (M − 1) 299.2406, found 299.2403.

4a. ^{1}H NMR: δ 3.09 (m, 1 H), 2.72 (m, 1 H), 1.90 (d, J = 3.1 Hz, 1 H), 1.59–1.25 (m, 18 H), 0.93–0.83 (2 m, 6 H), 0.17 (s, 9 H). ^{13}C NMR: δ 80.49, 62.66, 61.06, 35.58, 32.08, 30.48, 29.72, 29.33, 27.58, 23.30, 20.12, 14.18, 0.01. IR: 3460 cm^{-1}. Exact mass calcd for $C_{16}H_{33}O_2Si$ (M − 15) 285.2250, found 285.2242.

Metalation of 2c and Reaction with Butanal. By use of the general procedure, metalation of **2c** (285 mg, 1.25 mmol) and subsequent reaction with butanal afforded **(4R*,5S*,6S*)-5,6-epoxy-5-(trimethylsilyl)tetradecan-4-ol (3c)** (75 mg, 0.250 mmol, 20%, R_f = 0.28) and **(4R*,5R*,6R*)-5,6-epoxy-5-(trimethylsilyl)tetradecan-4-ol (4c)** (162 mg, 0.537 mmol, 43%, R_f = 0.12) after flash chromatography on silica gel (20:1 hexanes–EtOAc).

3c. ^{1}H NMR: δ 3.78 (m, 1 H), 2.79 (m, 1 H), 1.86 (d, J = 2.2 Hz, 1 H), 1.75–1.25 (m, 18 H), 0.93–0.86 (2 m, 6 H), 0.07 (s, 9 H). ^{13}C NMR: δ 71.08, 60.89, 58.77, 36.68, 31.85, 29.57, 29.53, 29.19, 28.37, 27.29, 22.64, 19.80, 14.01, 13.97, −2.39. IR: 3490 cm^{-1}. Exact mass calcd for $C_{17}H_{35}OSi$ (M − 17) 283.2457, found 283.2473.

4c. ^{1}H NMR: δ 3.52 (m, 1 H), 2.83 (m, 1 H), 1.85 (d, J = 1.9 Hz, 1 H), 1.66–1.26 (m, 18 H), 0.94–0.87 (2 m, 6 H), 0.10 (s, 9 H). ^{13}C NMR: δ 75.77, 61.49, 61.28, 35.83, 31.83, 29.53, 29.49, 29.17, 28.54, 27.33, 22.63, 19.49, 14.00, 13.88, −1.67. IR: 3480 cm^{-1}. Exact mass calcd for $C_{17}H_{35}OSi$ (M − 17) 283.2457, found 283.2426.

Metalation of 2d and Reaction with Butanal. By use of the general procedure, metalation of **2d** (282 mg, 1.32 mmol) and subsequent reaction with butanal afforded **(4R*,5S*,6S*)-5,6-epoxy-5-(trimethylsilyl)tridecan-4-ol (3d)** (97 mg, 0.338 mmol, 26%, R_f = 0.51 with 8:1 hexanes–EtOAc) and **(4R*,5S*,6R*)-5,6-epoxy-5-(trimethylsilyl)tridecan-4-ol (4d)** (178 mg, 0.621 mmol, 47%, R_f = 0.44 with 8:1 hexanes–EtOAc) after flash chromatography on silica gel (20:1 hexanes–EtOAc).

3d. ^{1}H NMR: δ 3.77 (m, 1 H), 2.81 (m, 1 H), 1.89 (d, J = 2.2 Hz, 1 H), 1.75–1.25 (m, 16 H), 0.95–0.85 (2 m, 6 H), 0.06 (s, 9 H). ^{13}C NMR: δ 90.57, 63.16, 59.80, 35.10, 31.79, 29.65, 29.35, 27.57, 27.15, 22.64, 14.08, 1.02. IR: 3500 cm^{-1}. Exact mass calcd for $C_{16}H_{33}O_2Si$ (M − 1) 285.2250, found 285.2254.

4d. ^{1}H NMR: δ 3.50 (m, 1 H), 2.81 (m, 1 H), 2.20 (s, 1 H), 1.67–1.25 (m, 16 H), 0.92–0.82 (2 m, 6 H), 0.08 (s, 9 H). ^{13}C NMR: δ 75.30, 61.75, 60.86, 35.35, 31.32, 29.15, 28.77, 28.12, 26.98, 22.25, 19.05, 13.95, 13.78, −2.04. IR: 3450 cm^{-1}. Exact mass calcd for $C_{16}H_{33}O_2Si$ (M − 1) 285.2250, found 285.2272.

Metalation of 2g and Reaction with Butanal. A solution of **2g** (319 mg, 1.73 mmol) and TMEDA (0.30 mL, 1.99 mmol) in 40 mL of Et_2O was cooled to −116 °C and treated with *sec*-butyllithium (2.5 mL, 2.0 mmol, 0.8 M in cyclohexane). After 3 h at −116 °C, a solution of butanal (0.2 mL, 2.27 mmol) in 10 mL of diethyl ether (cooled to −116 °C) was added. After warming to room temperature the mixture was poured into 10 mL of saturated ammonium chloride solution. The organic layer was separated, washed with brine, dried over magnesium sulfate, and concentrated. Flash chromatography on silica gel (20:1 hexanes–EtOAc) afforded **(R*,S*)-2-(1-hydroxybutyl)-2-(trimethylsilyl)oxaspiro[2.5]octane (3g)** (149 mg, 0.581 mmol, 34%, R_f = 0.16) as a colorless solid, mp 67–69 °C, and **(R*,R*)-2-(1-hydroxybutyl)-2-(trimethylsilyl)oxaspiro[2.5]octane (4g)** (96.6 mg, 0.377 mmol, 22%, R_f = 0.01).

3g. ^{1}H NMR: δ 4.01 (m, 1 H), 2.29 (s, 1 H), 2.05–1.37 (m, 14 H), 0.93 (m, 3 H), 0.14 (s, 9 H). ^{13}C NMR: δ 69.85, 66.49, 65.00, 35.26, 34.72, 30.98, 25.64, 24.78, 20.01, 13.97, −0.09. IR: 3490 cm^{-1}. Exact mass calcd for $C_{14}H_{27}OSi$ (M − 17) 239.1831, found 239.1776.

4g. ^{1}H NMR: δ 3.64 (m, 1 H), 1.85 (d, J = 2.7 Hz, 1 H), 1.63–1.28 (m, 14 H), 0.91 (m, 3 H), 0.19 (s, 9 H). ^{13}C NMR: δ 75.40, 67.93, 66.98, 35.29, 34.34, 31.20, 25.86, 24.97, 24.81, 19.33, 14.02, 1.46. IR 3490 cm^{-1}. Exact mass calcd for $C_{14}H_{27}O_2Si$ (M − 1) 255.1780, found 255.1778.

Metalation of 2a and Reaction with 2-Methylpropanal (6a). By use of the general procedure, metalation of **2a** (250 mg, 1.09 mmol) and subsequent reaction with **6a** afforded two diastereomers, **(3R*,4S*,5R*)-4,5-epoxy-2-methyl-4-(trimethylsilyl)tridecan-3-ol (7a)** and **(3R*,4R*,5S*)-4,5-epoxy-2-methyl-4-(trimethylsilyl)tridecan-3-ol (8a),** in a 2.4: 1 ratio. The products (240 mg, 0.799 mmol, 73%) could be isolated by Kugelrohr distillation (bp 95 °C/0.05 mmHg), but separation of the isomers required flash chromatography on silica gel (30:1 hexanes–EtOAc).

7a. ^{1}H NMR: δ 3.75 (m, 1 H), 3.15 (m, 1 H), 1.95 (m, 1 H), 1.88–1.28 (m, 15 H), 1.09–0.83 (m, 9 H), 0.15 (s, 9 H). ^{13}C NMR: δ 73.32, 58.07, 57.92, 31.75, 29.70, 29.46, 29.18, 26.81, 22.76, 20.89, 14.73, 14.08, −1.20. IR: 3500 cm^{-1}. Exact mass calcd for $C_{17}H_{35}O_2Si$ (M − 1) 299.2406, found 299.2411.

8a. ^{1}H NMR: δ 2.71 (m, 1 H), 2.56 (m, 1 H), 1.98 (d, J = 2.7 Hz, 1 H), 1.88–1.25 (m, 15 H), 1.00–0.83 (m, 9 H), 0.18 (s, 9 H). ^{13}C NMR: δ 86.31, 64.08, 60.37, 31.72, 30.82, 28.03, 27.80, 26.99, 22.64, 19.76, 19.37, 14.00, −1.12. IR: 3490 cm^{-1}. Exact mass calcd for $C_{17}H_{35}O_2Si$ (M − 1) 299.2406, found 299.2403.

Metalation of 2a and Reaction with 2,2-Dimethylpropanal (6b). By use of the general procedure, metalation of **2a** (300 mg, 1.31 mmol) and subsequent reaction with **6b** afforded **(3R*,4S*,5R*)-2,2-dimethyl-4,5-epoxy-4-(trimethylsilyl)tridecan-3-ol (7b)** (226 mg, 0.718 mmol, 55%, R_f = 0.35) and **(3R*,4R*,5S*)-2,2-dimethyl-4,5-epoxy-4-(trimethylsilyl)tridecan-3-ol (8b)** (114 mg, 0.362 mmol, 28%, R_f = 0.10) in a 2:1 ratio after flash chromatography on silica gel (30:1 hexanes–EtOAc).

7b. ^{1}H NMR: δ 3.60 (s, 1 H), 3.16 (m, 1 H), 2.75 (s, 1 H), 1.63–1.25 (m, 14 H), 0.94 (s, 9 H), 0.89–0.85 (m, 3 H), 0.16 (s, 9 H). ^{13}C NMR: δ 74.99, 58.64, 56.79, 34.83, 31.60, 29.90, 29.73, 29.18, 27.00, 26.82, 22.56, 13.73, 0.02. IR: 3495 cm^{-1}. Exact mass calcd for $C_{18}H_{36}O_2Si$ (M − 1) 313.2562, found 313.2570.

8b. ^{1}H NMR: δ 2.74 (2 m, 2 H), 1.95 (d, J = 3.8 Hz, 1 H), 1.63–1.25 (m, 14 H), 0.97 (s, 9 H), 0.89–0.83 (m, 3 H), 0.20 (s, 9 H). ^{13}C NMR: δ 70.80, 60.88, 58.66, 36.40, 31.44, 29.28, 29.04, 28.14, 27.24, 22.56, 19.74, 14.03, −2.44. IR: 3500 cm^{-1}. Exact mass calcd for $C_{18}H_{37}O_2Si$ (M − 1) 313.2562, found 313.2569.

Metalation of 2a and Reaction with Benzaldehyde (6c). By use of the general procedure, metalation of **2a** (235 mg, 1.03 mmol) and subsequent reaction with **6c** (153 mg, 1.44 mmol) afforded an inseparable 7.7:1 mixture of **(3R*,4S*,5R*)-2,3-epoxy-1-phenyl-2-(trimethylsilyl)undecan-1-ol (7c)** and **(3R*,4R*,5S*)-2,3-epoxy-1-phenyl-2-(trimethylsilyl)undecan-1-ol (8c)** (251 mg, 0.750 mmol, 73%) after Kugelrohr distillation, bp 120 °C (0.05 mmHg). ^{1}H NMR: δ 7.34 (m, 5 H), 4.82 (s, 1 H), 4.42 (m, 1 H, **8c**), 3.54 (m, 1 H), 2.96 (m, 1 H, **8c**), 2.63 (s, 1 H), 2.47 (m, 1 H, **8c**), 1.70–1.27 (m, 14 H), 0.88 (m, 3 H), −0.04 (s, 9 H, **8c**), −0.06 (s, 9 H). ^{13}C NMR: δ 138.08, 127.17, 127.01, 126.19 (**8c**), 125.55 (**8c**), 124.40 (**8c**), 78.22 (**8c**), 77.23 (**8c**), 71.01, 61.12 (**8c**), 56.71, 30.18, 28.27, 28.00, 27.63, 25.59, 21.10, 12.64, −1.71 (**8c**), −2.55. IR: 3480 cm^{-1}. Exact mass calcd for $C_{20}H_{33}O_2Si$ (M − 1) 333.2250, found 333.2252.

Metalation of 2a and Reaction with Crotonaldehyde (6d). By use of the general procedure, metalation of **2a** (282 mg, 1.23 mmol) and subsequent reaction with **6d** (0.15 mL, 1.81 mmol) afforded a 4:1 mixture of **(E)-(4R*,5S*,6R*)-5,6-epoxy-5-(trimethylsilyl)-2-tetradecen-4-ol (7d)** and **(E)-(4R*,5R*,6S*)-5,6-epoxy-5-(trimethylsilyl)-2-tetradecen-4-ol (8d)** in 72% yield, which could partially be separated by flash chromatography on silica gel (20:1 hexanes–EtOAc) to give **7d** (182 mg, 0.610 mmol, 50%, R_f = 0.19) and **8d** (42.0 mg, 0.141 mmol, 11%, R_f = 0.07).

7d. ^{1}H NMR: δ 5.82 (ddd, J = 15.8, 13.0, 6.5 Hz, 1 H), 5.28 (ddd, J = 15.8, 8.1, 1.3 Hz, 1 H), 4.22 (d, J = 8.1 Hz, 1 H), 3.08 (m, 1 H), 2.34 (s, 1 H), 1.71 (dd, J = 6.5, 1.3 Hz, 3 H), 1.67–1.25 (m, 14 H), 0.85 (m, 3 H), 0.10 (s, 9 H). ^{13}C NMR: δ 130.74, 129.28, 70.09, 57.65, 57.34, 31.37, 29.58, 29.22, 28.92, 26.85, 22.26, 17.48, 13.73, −1.31. IR: 3480 cm^{-1}. Exact mass calcd for $C_{17}H_{33}OSi$ (M − 17) 281.2301, found 281.2291.

8d. ^{1}H NMR: δ 5.77–5.39 (m, 2 H), 3.75 (m, 1 H), 2.79 (m, 1 H), 2.16 (d, J = 3.2 Hz, 1 H), 1.69 (dd, J = 3.2, 1.2 Hz, 3 H), 1.64–1.24 (m, 14 H), 0.85 (m, 3 H), 0.14 (s, 9 H). ^{13}C NMR: δ 129.89, 128.28, 79.20, 61.55, 59.30, 31.71, 29.78, 29.30, 29.25, 26.57, 22.08, 17.26, 13.74, −0.38. IR: 3410 cm^{-1}. Exact mass calcd for $C_{17}H_{33}O_2Si$ (M − 1) 297.2250, found 297.2246.

Metalation of 2a and Reaction with Phenylpropynal (6e). By use of the general procedure, metalation of **2a** (280 mg, 1.23

mmol) and subsequent reaction with **6e** (0.19 mL, 1.55 mmol) afforded an inseparable 2.5:1 mixture of **(3*R**,4*S**,5*R**)-4,5-epoxy-1-phenyl-4-(trimethylsilyl)-1-tridecyn-3-ol (7e)** and **(3*R**,4*R**,5*S**)-4,5-epoxy-1-phenyl-4-(trimethylsilyl)-1-tridecyn-3-ol (8e)** (200 mg, 0.558 mmol, 45%) after Kugelrohr distillation, bp 120 °C (0.04 mmHg). ^{1}H NMR: δ 7.44–7.27 (m, 5 H), 4.74 (s, 1 H), 4.26 (m, 1 H, **8e**), 3.27 (m, 1 H), 3.00 (m, 1 H, **8e**), 2.40 (s, 1 H), 2.22 (m, 1 H, **8e**), 1.69–1.25 (m, 14 H), 0.85 (m, 3 H), 0.34 (s, 9 H, **8e**), 0.27 (s, 9 H). ^{13}C NMR: δ 131.55, 128.46 (**8e**), 128.14, 122.34 (**8e**), 86.81, 86.48 (**8e**), 69.42, 62.19 (**8e**), 61.67, 59.49 (**8e**), 58.31, 58.17, 31.77, 30.05, 29.94, 29.43, 29.11, 27.05, 22.56, 14.00, –0.36 (**8e**), –1.28. IR: 3445, 2229, 2231 cm^{-1}. Exact mass calcd for $C_{22}H_{33}OSi$ (M – 17) 341.2301, found 341.2312.

Metalation of 2a and Reaction with (±)-2-Phenylpropanal (6f). By use of the general procedure, metalation of **2a** (286 mg, 1.25 mmol) and subsequent reaction with **6f** afforded 66% of an inseparable mixture of 4 diastereomers of **4,5-epoxy-2-phenyl-4-(trimethylsilyl)tridecan-3-ol**. Two diastereomers could be isolated by flash chromatography on silica gel (20:1 hexanes–EtOAc): diastereomer A (40 mg, 0.110 mmol, 9%, R_f = 0.20) and diastereomer B (40 mg, 0.110 mmol, 9%, R_f = 0.14).

Diastereomer A. ^{1}H NMR: δ 7.36–7.17 (m, 5 H), 4.04 (m, 1 H), 3.26 (m, 1 H), 2.93 (m, 1 H), 2.03 (s, 1 H), 1.68–1.27 (m, 14 H), 1.23 (d, J = 7.1 Hz, 3 H), 0.85 (m, 3 H), 0.20 (s, 9 H). ^{13}C NMR: δ 145.26, 128.23, 127.63, 126.35, 72.88, 58.09, 57.72, 41.46, 31.85, 29.98, 29.49, 29.20, 27.11, 22.64, 14.08, 13.70, –1.01. IR: 3490 cm^{-1}. Exact mass calcd for $C_{22}H_{37}O_2Si$ (M – 1) 361.2563, found 361.2588.

Diastereomer B. ^{1}H NMR: δ 7.24–7.17 (m, 5 H), 3.14 (m, 1 H), 2.94 (m, 1 H), 2.41 (d, J = 2.9 Hz, 1 H), 2.19 (m, 1 H), 1.33 (d, J = 6.7 Hz, 1 H), 1.32–1.25 (m, 14 H), 0.86 (m, 3 H), 0.18 (s, 9 H). ^{13}C NMR: δ 144.18, 128.33, 127.87, 126.57, 86.81, 64.68, 60.42, 42.84, 31.82, 30.06, 29.30, 29.23, 29.11, 26.24, 22.64, 19.71, 14.11, 0.70. IR: 3505 cm^{-1}. Exact mass calcd for $C_{22}H_{37}O_2Si$ (M – 1) 361.2563, found 361.2588.

Metalation of 2a and Reaction with (*S*)-2,2-Dimethyl-4-formyl-1,3-dioxolane. By use of the general procedure, metalation of **2a** (281 mg, 1.23 mmol) and subsequent reaction with (*S*)-2,2-dimethyl-4-formyl-1,3-dioxolane afforded 69% of **(2*S*)-2,2-dimethyl-α-[3-octyl-2-(trimethylsilyl)oxiranyl]-1,3-dioxolane-4-methanol** as an inseparable mixture of four diastereomers. Two diastereomers could be isolated by flash chromatography on silica gel (15:1 hexanes–EtOAc): diastereomer C (76 mg, 0.212 mmol, 17%, R_f = 0.07) and diastereomer D (80 mg, 0.223 mmol, 18%, R_f = 0.02).

Diastereomer C. ^{1}H NMR: δ 4.07 (m, 1 H), 3.82 (m, 3 H), 3.00 (m, 1 H), 3.36 (s, 1 H), 1.55–1.25 (m, 14 H), 1.40 (s, 3 H), 1.33 (s, 3 H), 0.86 (m, 3 H), 0.15 (s, 9 H). ^{13}C NMR: δ 109.34, 77.72, 70.04, 67.82, 57.74, 57.20, 31.85, 29.94, 29.49, 29.19, 26.94, 26.32, 25.39, 22.66, 14.10, –0.89. IR: 3490 cm^{-1}.

Diastereomer D. ^{1}H NMR: δ 4.09 (m, 2 H), 3.83 (m, 1 H), 3.22 (m, 1 H), 2.83 (m, 1 H), 2.53 (m, 1 H), 1.50–1.24 (m, 14 H), 1.35 (s, 3 H), 1.30 (s, 3 H), 0.85 (m, 3 H), 0.17 (s, 9 H). ^{13}C NMR: δ 108.85, 80.77, 75.63, 67.38, 63.21, 59.07, 31.85, 29.90, 29.46, 29.16, 26.94, 26.82, 25.05, 22.66, 14.08, –0.22. IR: 3470 cm^{-1}. Exact mass calcd for $C_{19}H_{37}O_4Si$ (M – 1) 357.2461, found 357.2480.

1-(Trimethylstannyl)-1-(trimethylsilyl)-1,2-epoxydecane. By use of the general procedure, metalation of **2a** (283 mg, 1.23 mmol) and subsequent reaction with bromotrimethylstannane afforded (412 mg, 1.05 mmol, 85%) of the desired epoxide after Kugelrohr distillation; bp 90 °C (0.05 mmHg). ^{1}H NMR: δ 3.01 (m, 1 H), 1.45–1.25 (m, 14 H), 0.85 (m, 3 H), 0.08 (2 s, 18 H). ^{13}C NMR: δ 62.18, 56.82, 32.31, 31.85, 29.57, 29.19, 27.30, 22.66, 14.08, –0.36, –9.46. IR: 2940 cm^{-1}.

Desilylation of 1,2-Epoxysilanes: General Procedure. Tetrabutylammonium fluoride trihydrate (7.66 mg, 2.43 mmol) was added to a solution of 2.00 mmol of 1,2-epoxysilane in 20 mL of DMSO and stirred at room temperature for 3 h. The reaction mixture was poured into 10 mL of water and extracted with hexanes (3×). The combined organic extracts were washed with brine, dried, concentrated, and Kugelrohr distilled.

(4*R,5*R**,6*R**)-5,6-Epoxytetradecan-4-ol (9a).** By use of the general procedure the desilylation of **3a** (600 mg, 2.00 mmol) afforded **9a** (357 mg, 1.56 mmol, 79%), bp 90 °C (0.05 mmHg). ^{1}H NMR: δ 3.77 (m, 1 H), 2.97 (m, 1 H), 2.73 (m, 1 H), 1.95 (s, 1 H), 1.58–1.26 (m, 18 H), 0.97–0.83 (2 m, 6 H). ^{13}C NMR: δ 68.70, 60.91, 54.91, 35.50, 31.73, 31.54, 29.43, 29.18, 25.98, 22.60, 18.58, 14.11. Exact mass calcd for $C_{14}H_{26}O_2$ (M – 2) 226.1932, found 226.1932.

(4*R,5*S**,6*S**)-5,6-Epoxytetradecan-4-ol (10a).** By use of the general procedure the desilylation of **4a** (400 mg, 1.33 mmol) afforded **10a** (266 mg, 1.17 mmol, 88%), bp 90 °C (0.05 mmHg). ^{1}H NMR: δ 3.43 (m, 1 H), 2.88 (m, 1 H), 2.79 (m, 1 H), 1.96 (m, 1 H), 1.64–1.24 (m, 18 H), 0.95–0.82 (2 m, 6 H). ^{13}C NMR: δ 72.12, 61.87, 57.08, 36.46, 31.67, 31.54, 29.24, 29.11, 25.79, 22.54, 18.39, 13.92. IR: 3460 cm^{-1}. Exact mass calcd for $C_{14}H_{26}O_2$ (M – 2) 226.1932, found 226.1933.

Metalation of 2f, Reaction with Butanal, and Desilylation. By use of the general procedure, metalation of **2f** (397 mg, 0.957 mmol) and reaction with butanal was carried out, providing a crude epoxy alcohol product. By the general procedure for the desilylation of epoxysilanes, the reaction of this crude intermediate afforded a 1.3:1 mixture of **9a**:**10a** (179 mg, 0.784 mmol, 82%) after Kugelrohr distillation.

Swern Oxidation of Epoxy Alcohols: General Procedure. To a solution of oxalyl chloride (0.31 g, 2.44 mmol) in 8 mL of CH_2Cl_2 at –78 °C was slowly added DMSO (0.39 g, 4.99 mmol). After 2 min 1.24 mmol of the epoxy alcohol in 2 mL of CH_2Cl_2 was added. After another 15 min Et_3N (1.40 mL, 10.0 mmol) was added, and the reaction mixture was stirred at –78 °C for 15 min and at room temperature for additional 30 min. The reaction mixture was poured into water and extracted with hexanes (3×), dried, concentrated, and Kugelrohr distilled.

***trans*-5,6-Epoxytetradecan-4-one (11a).** By use of the general procedure the oxidation of **9a** (283 mg, 1.24 mmol) afforded **11a** (177 mg, 0.782 mmol, 63%), bp 120 °C (0.2 mmHg). ^{1}H NMR: δ 3.17 (m, 1 H), 2.99 (m, 1 H), 2.30 (m, 2 H), 1.64–1.24 (m, 16 H), 0.91–0.85 (2 m, 6 H). ^{13}C NMR: δ 192.36, 61.05, 58.95, 40.37, 33.17, 30.66, 30.38, 26.96, 23.28, 17.73, 15.29, 14.80. IR 1720 cm^{-1}. Exact mass calcd for $C_{14}H_{26}O_2$ (M$^+$) 226.1933, found 226.1935.

***cis*-5,6-Epoxytridecan-4-one (11d).** By use of the general procedure for the desilylation and oxidation, a mixture of **3d** and **4d** (569 mg, 1.99 mmol) afforded **11d** (333 mg, 1.57 mmol, 79%) after Kugelrohr distillation, bp 65 °C (0.05 mmHg). ^{1}H NMR: δ 3.54 (m, 1 H), 3.15 (m, 1 H), 2.48 (m, 2 H), 1.66–1.08 (m, 14 H), 0.98–0.81 (2 m, 6 H). ^{13}C NMR: δ 206.13, 58.33, 42.92, 31.69, 29.54, 29.21, 27.44, 26.26, 22.59, 16.63, 14.09, 13.67. IR: 1720 cm^{-1}. Exact mass calcd for $C_{13}H_{24}O_2$ (M$^+$) 212.1776, found 212.1775.

Reduction of Epoxy Ketones 11. Sodium borohydride (27.2 mg, 0.720 mmol) was added to 3 mL of CH_3OH at 0 °C, and a cooled solution of 0.720 mmol of epoxy ketone in 3 mL of CH_3OH was subsequently added. The mixture was stirred for 35 min at 0 °C; 5 mL of 8% HCl was added, and the resulting solution was extracted with Et_2O (3×). The combined organic extracts were washed with brine, dried, concentrated, and distilled.

Reduction of **11a** (163 mg, 0.720 mmol) gave an 84:16 mixture of **9a**:**10a** (130 mg, 0.569 mmol, 79%).

Reduction of **11d** (133 mg, 0.626 mmol) gave a 92:8 mixture of **9d**:**10d** (120 mg, 0.560 mmol, 89%).

***cis*-3,4-Epoxy-2-phenyl-3-(trimethylsilyl)dodecan-2-ol (14).** By use of the general procedure, metalation of **2a** (283 mg, 1.24 mmol) and subsequent reaction with acetophenone afforded two diastereomers, a minor diastereomer (35 mg, 0.100 mmol, 8%) and a major diastereomer (319 mg, 0.906 mmol, 73%), after flash chromatography on silica gel (20:1 hexanes–EtOAc).

Minor Diastereomer. ^{1}H NMR: δ 7.48–7.23 (m, 5 H), 3.23 (m, 1 H), 2.26 (s, 1 H), 1.72–1.28 (m, 14 H), 1.43 (s, 3 H), 0.87 (m, 3 H), –0.15 (s, 9 H). ^{13}C NMR: δ 145.80, 128.25, 127.25, 125.59, 75.65, 62.37, 60.42, 31.90, 30.44, 29.62, 29.27, 27.58, 25.37, 22.90, 14.16, 0.55. IR: 3480 cm^{-1}. Exact mass calcd for $C_{21}H_{35}O_2Si$ (M – 1) 347.2406, found 347.2398.

Major Diastereomer. ^{1}H NMR: δ 7.48–7.26 (m, 5 H), 3.47 (m, 1 H), 2.13 (s, 1 H), 1.64 (s, 3 H), 1.63–1.26 (m, 14 H), 0.87 (m, 3 H), –0.10 (s, 9 H). ^{13}C NMR: δ 143.34, 127.92, 128.06, 126.71, 75.27, 62.16, 59.85, 31.82, 30.00, 29.57, 29.19, 27.46, 25.61, 22.64, 14.08, 0.75. IR: 3475 cm^{-1}. Exact mass calcd for $C_{21}H_{35}O_2Si$ (M – 1) 347.2406, found 347.2406.

***cis*-4,5-Epoxy-2,2,3-trimethyl-4-(trimethylsilyl)tridecan-3-ol (15).** By use of the general procedure, metalation of **2a** (290 mg, 1.27 mmol) and subsequent reaction with 3,3-dimethylbutanone afforded the carbonyl addition product (233 mg, 0.711 mmol, 56%) as a single diastereomer after flash chromatography on silica gel (30:1 hexanes–EtOAc). ^{1}H NMR: δ 3.25 (m, 1 H), 2.41 (s, 1 H), 1.56 (s, 1 H), 1.6–1.24 (m, 14 H), 1.19 (s, 3 H), 0.97 (s, 9 H), 0.85 (m, 3 H), 0.21 (s, 9 H). ^{13}C NMR: δ 78.44, 60.83, 57.63, 37.26, 31.85, 31.60, 29.52, 29.22, 27.32, 27.05, 26.81, 24.07, 22.66, 14.08, 2.41. IR: 3520 cm^{-1}. Exact mass calcd for $C_{19}H_{39}O_2Si$ (M − 1) 327.2719, found 327.2707.

1-[3-Octyl-2-(trimethylsilyl)oxiranyl]-2-cyclohexen-1-ol (16). By use of the general procedure, metalation of **2a** (281 mg, 1.23 mmol) and subsequent reaction with 2-cyclohexen-1-one afforded an inseparable 9:1 mixture of two diastereomers (E and F, 309 mg, 0.972 mmol, 79%) after flash chromatography on silica gel (20:1 hexanes–EtOAc). ^{1}H NMR: δ 5.80 (m, 1 H), 5.63 (m, 1 H), 5.54 (m, 1 H, F), 5.50 (m, 1 H, F), 3.23 (m, 1 H), 2.90 (m, 1 H, F), 2.26 (s, 1 H, F), 2.13 (s, 1 H), 2.08–1.25 (m, 20 H), 0.86 (m, 3 H), 0.18 (s, 9 H, F), 0.13 (s, 9 H). ^{13}C NMR: δ 130.98, 130.63 (F), 129.25, 128.63 (F), 72.83 (F), 69.33, 62.39 (F), 61.03, 60.04 (F), 58.52, 33.55 (F), 31.73, 29.79, 29.37, 29.12, 27.27, 24.94, 22.52, 18.09 (F), 18.05, 13.94, 1.00 (F), 0.73. IR: 3480 cm^{-1}. Exact mass calcd for $C_{19}H_{35}O_2Si$ (M − 1) 323.2406, found 323.2405.

3-Octyl-2-(trimethylsilyl)-α-methyl-α-(1-cyclohexen-1-yl)oxirane-2-methanol (17). By use of the general procedure, metalation of **2a** (281 mg, 1.23 mmol) and subsequent reaction with 1-acetylcyclohexene afforded two diastereomeric carbonyl addition products after flash chromatography on silica gel (25:1 hexanes–EtOAc): major diastereomer (157 mg, 0.445 mmol, 36%, R_f = 0.14), minor diastereomer (63.0 mg, 0.179 mmol, 15%, R_f = 0.09), and 40 mg of a mixture of both diastereomers.

Major Diastereomer. ^{1}H NMR: δ 5.74 (m, 1 H), 3.05 (m, 1 H), 2.00 (m, 5 H), 1.63–1.26 (m, 18 H), 1.19 (s, 3 H), 0.86 (m, 3 H), 0.11 (s, 9 H). ^{13}C NMR: δ 140.82, 122.56, 75.78, 61.62, 59.18, 31.79, 30.30, 29.52, 29.14, 27.38, 25.05, 24.32, 22.77, 22.56, 22.04, 14.05, 0.83. IR: 3500 cm^{-1}. Exact mass calcd for $C_{21}H_{39}O_2Si$ (M − 1) 351.2719, found 351.2709.

Minor Diastereomer. ^{1}H NMR: δ 5.78 (m, 1 H), 3.31 (m, 1 H), 2.06 (m, 4 H), 1.84 (s, 1 H), 1.62–1.25 (m, 18 H), 1.35 (s, 3 H), 0.86 (m, 3 H), 0.11 (s, 9 H). ^{13}C NMR: δ 138.76, 125.13, 75.56, 61.02, 60.26, 31.85, 30.03, 29.52, 29.19, 27.48, 25.29, 24.80, 24.23, 22.74, 22.66, 22.09, 14.08, 1.05. IR: 3490 cm^{-1}. Exact mass calcd for $C_{21}H_{39}O_2Si$ (M − 1) 351.2719, found 351.2719.

4-*tert*-Butyl-1-[3-octyl-2-(trimethylsilyl)oxiranyl]cyclohexanol (18). By use of the general procedure, metalation of **2a** (373 mg, 1.63 mmol) and subsequent reaction with 4-*tert*-butylcyclohexanone afforded the carbonyl addition product (350 mg, 0.915 mmol, 56%) after flash chromatography on silica gel (25:1 hexanes–EtOAc, R_f = 0.17). ^{1}H NMR: δ 3.16 (m, 1 H), 1.65–1.25 (m, 23 H), 0.86 (m, 3 H), 0.83 (s, 9 H), 0.19 (s, 9 H); ^{13}C NMR: δ 72.50, 62.70, 59.50, 47.75, 35.72, 33.49, 32.44, 31.83, 29.88, 29.56, 29.18, 27.54, 22.66, 22.25, 14.08, 1.51. IR: 3470 cm^{-1}. Exact mass calcd for $C_{23}H_{45}O_2Si$ (M − 1) 381.3189, found 381.3190.

4-Methyl-1-[3-octyl-2-(trimethylsilyl)oxiranyl]cyclohexanol (19). By use of the general procedure, metalation of **2a** (282 mg, 1.23 mmol) and subsequent reaction with 4-methylcyclohexanone afforded an inseparable 1.5:1 mixture of diastereomeric carbonyl addition products (320 mg, 0.939 mmol, 76%) after Kugelrohr distillation, bp 120 °C (0.05 mmHg). ^{1}H NMR: δ 3.15 (m, 1 H), 1.83–1.24 (m, 23 H), 0.94–0.82 (2 m, 6 H), 0.19 (s, 9 H), 0.17 (s, 9 H). ^{13}C NMR: δ 73.10, 72.26, 62.80, 62.77, 60.13, 59.30, 35.04, 32.85, 32.13, 31.77, 30.84, 29.94, 29.76, 29.62, 29.45, 29.14, 28.60, 27.92, 27.57, 27.32, 27.21, 22.58, 22.37, 18.28, 14.00, 1.42, 1.35. IR: 3480 cm^{-1}. Exact mass calcd for $C_{20}H_{39}O_2Si$ (M − 1) 339.2719, found 339.2721.

Dihydro-5-methyl-5-[3-octyl-2-(trimethylsilyl)oxiranyl]-2(3*H*)-furanone (20). By use of the general procedure, metalation of **2a** (282 mg, 1.23 mmol) and subsequent reaction with ethyl levulinate afforded two diastereomers, a minor diastereomer (10 mg, 0.031 mmol, 2%) and a major diastereomer (30.0 mg, 0.092 mmol, 7%), along with a 1:1.5 mixture of both (115 mg, 0.352 mmol, 29%) after flash chromatography on silica gel (15:1 hexanes–EtOAc).

Minor Diastereomer. ^{1}H NMR: δ 2.57–2.46 (m, 4 H), 2.13 (m, 1 H), 1.61–1.25 (m, 15 H), 1.43 (s, 3 H), 0.86 (m, 3 H), 0.21 (s, 9 H). ^{13}C NMR: δ 176.27, 90.35, 60.19, 59.52, 31.87, 29.48, 29.17, 28.98, 27.56, 27.23, 25.64, 22.63, 14.12, 0.51. IR: 1790 cm^{-1}. Exact mass calcd for $C_{18}H_{34}O_3Si$ (M$^+$) 326.2277, found 326.2292.

Major Diastereomer. ^{1}H NMR: δ 3.17 (m, 1 H), 2.71–2.31 (m, 3 H), 2.01–1.90 (m, 1 H), 1.60–1.24 (m, 14 H), 1.45 (s, 3 H), 0.85 (m, 3 H), 0.17 (s, 9 H). ^{13}C NMR: δ 176.09, 86.41, 61.23, 59.28, 33.00, 32.01, 29.92, 29.63, 29.30, 29.24, 27.32, 24.87, 22.80, 14.21, 0.56. IR: 1790 cm^{-1}. Exact mass calcd for $C_{17}H_{31}O_2Si$ (M − 15) 311.2042, found 311.2054.

(1*R[2*S**,3*R**])-1-[3-*tert*-Butyl-2-(trimethylsilyl)oxiranyl]-2-cyclohexen-1-ol (21).** A solution of **2b** (219 mg, 1.27 mmol) and TMEDA (0.37 mL, 2.54 mmol) in 30 mL of Et_2O at −116 °C was treated with *s*-BuLi (1.95 mL, 2.54 mmol, 1.3 M in cyclohexane), and the resulting yellow mixture was stirred for 30 min at −116 °C. A solution of 2-cyclohexen-1-one (0.27 mL, 2.79 mmol) in 10 mL of Et_2O at −116 °C was added. The mixture was allowed to warm to room temperature, hydrolyzed with saturated NH_4Cl solution, washed with brine, dried, and concentrated. Flash chromatography on silica gel (45:1 hexanes–EtOAc) and sublimation at 30 °C (0.05 mmHg) afforded the carbonyl addition product (70.3 mg, 0.262 mmol, 21%). ^{1}H NMR: δ 5.77 (m, 2 H), 2.66 (s, 1 H), 2.23 (s, 1 H), 2.14–1.74 (m, 6 H), 1.08 (s, 9 H), 0.06 (s, 9 H). ^{13}C NMR: δ 133.00, 128.23, 71.08, 69.40, 66.99, 32.18, 31.88, 29.32, 24.70, 18.33, −0.60. IR: 3450, 3030 cm^{-1}. Exact mass calcd for $C_{15}H_{26}OSi$ (M − 18) 250.1753, found 250.1766.

Transmetalation of Oxiranyl Anion 5: General Procedure. A solution of **2a** (283 mg, 1.24 mmol) and TMEDA (0.22 mL, 1.49 mmol) in 30 mL of Et_2O at −116 °C was treated with *s*-BuLi (1.14 mL, 1.49 mmol, 1.3 M in cyclohexane), and the resulting yellow solution was stirred for 10 min at −116 °C. A solution containing 1.50 mmol of the transmetalating agent in Et_2O or THF was cooled to −116 °C for −100 °C (THF) and added to the solution of **5**. In the case of insoluble transmetalating agents, inverse addition was carried out. After the reaction times shown below, butanal (0.15 mL, 1.70 mmol) in 10 mL of Et_2O (cooled to −116 °C) was added. After being warmed to room temperature the mixture was poured into 10 mL of saturated NH_4Cl solution; the organic layer was separated, washed with brine, dried over anhydrous $MgSO_4$, and concentrated.

Transmetalation with $MgBr_2$ (solution in Et_2O, 10 min) afforded 85% of a 2:1 mixture of **3a**:**4a**.

Transmetalation with $ClTi(O\text{-}i\text{-}Pr)_3$ (solution in Et_2O, 10 min) afforded 37% of a 7.7:1 mixture of **3a**:**4a**.

Transmetalation with $ClTi(O\text{-}i\text{-}Pr)_3$ (solution in Et_2O, 1 min) afforded 51% of a 2:1 mixture of **3a**:**4a**.

Transmetalation with $ClTi(NEt_2)_3$ (solution in Et_2O, 10 min) afforded 62% of a 1.5:1 mixture of **3a**:**4a**.

Transmetalation with $CeCl_3$ (slurry in THF, inverse addition, 20 min) afforded 66% of a 2.5:1 mixture of **3a**:**4a**.

Transmetalation with CeI_3 (slurry in THF, inverse addition, 30 min) afforded 43% of a 2:1 mixture of **3a**:**4a**.

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Supplementary Material Available: X-ray crystallographic structural data for compounds whose structures were elucidated by X-ray diffractometry (10 pages). Ordering information is given on any current masthead page.