Acknowledgment. This research was supported in part by the Ministry of Education, Science, and Culture (Grand-in Aid for Scientific Research Nos. 63106003, 63607502, and 63790207). One of us (K. Sato) thanks the Japan Society for Promotion of Science for the Fellowship for Japan Junior Scientists.

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(16) A similar trend was observed in the reaction of 3-hydroxy-2-butanone (**9**) with **2E** and **3**, although the stereoselectivity between the two hydroxy-substituted carbons was lowered. The major vs minor product ratios were 84/16 and 66/34, respectively, as determined by means of ^{1}H NMR and capillary GLC.

Organoaluminum-Promoted Rearrangement of Epoxy Silyl Ethers to β-Siloxy Aldehydes

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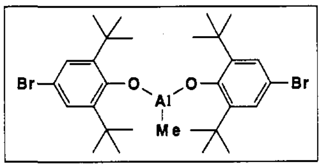
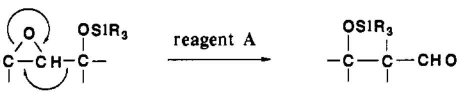
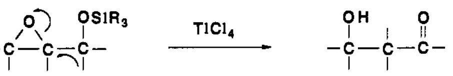
Reported herein is a new and highly effective method for converting epoxy silyl ethers to β-siloxy aldehydes by a bulky organoaluminum reagent (eq 1), which should find widespread use in organic synthesis.[1] Used in combination with the Sharpless asymmetric epoxidation of allylic alcohols,[2] this rearrangement represents a new approach to the synthesis of optically active β-hydroxy aldehydes, useful intermediates in natural product synthesis.[3] Several examples of this transformation are given in Table I. This method complements our previously reported rearrangement of epoxy silyl ethers to aldol products (eq 2).[4,5]





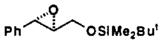
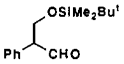
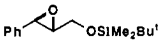
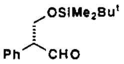
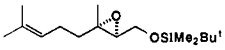
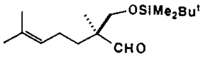
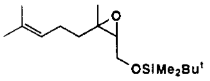
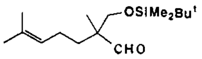
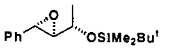
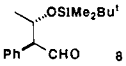
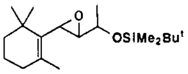
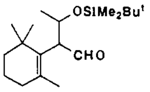
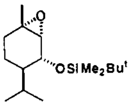
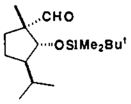
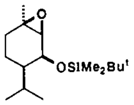
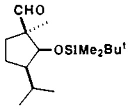
(1)



(2)

When the optically active epoxy *tert*-butyldimethylsilyl ether **1** (95% ee)[2b] was treated with 2 equiv of methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (reagent A)[6] in CH_2Cl_2 at −78 °C for 1 h, the corresponding β-siloxy aldehyde **2** ($[\alpha]_D$ −30.8° (*c* 1.0, $CHCl_3$)) was obtained in 87% yield (entry 1). The optical purity and absolute configuration of **2** were determined from the optical rotation of 2-phenylpropanol[7] which was derived from **2** by the following sequences: (1) $NaBH_4$, MeOH; (2) MsCl, NEt_3, CH_2Cl_2; (3) PhSNa, THF-EtOH; (4) Raney Ni, EtOH; (5) Bu_4NF, THF.[8,9] Hence, this organoaluminum-promoted rearrangement proceeds with rigorous transfer of the chirality of **1**, and the observed stereoselectivity can be interpreted to arise from the anti migration of the siloxymethyl group to the epoxide moiety. Similarly, the enantiomeric epoxy silyl ether **3** was equally transformed to the enantiomeric β-siloxy aldehyde **4** (entry 2) under the same conditions. The *tert*-butyldimethylsilyl ether **5** of optically active epoxy geraniol[2b] also underwent clean rearrangement to aldehyde **6** (entry 3) without any loss of the optical purity.[10] The stereochemistry at the migrating siloxy carbon is rigorously retained in the rearrangement (entries 5–8). For example, the essentially pure erythro isomer **7** (>99%) of the op-

Table I. Organoaluminum-Promoted Rearrangement of Epoxy Silyl Ethers[a]

entry	epoxy silyl ether[b]	β-siloxy aldehyde	yield (%)[c]
1	 1	 2	87
2	 3	 4	85
3	 5	 6	99
4			98
5	 7	 8	87[d]
6			93[e,f]
7			88[g,h]
8			82[i,j]

[a] Unless otherwise stated, the reaction was carried out in CH_2Cl_2 using 2 equiv of the reagent A at −78 °C for several hours. [b] The optically active substrates are utilized except for the entries 4 and 6. [c] Isolated yield. [d] The authentic *erythro*- and *threo*-β-siloxy aldehydes were prepared in separate experiments by using erythro and threo mixtures of the racemic epoxy silyl ether. [e] The starting epoxy silyl ether (erythro/threo = 3:1) was prepared by the $VO(acac)_2$-catalyzed epoxidation with *t*-BuOOH. For the erythro/threo structural assignments, see: Rossiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. *Tetrahedron Lett.* **1979**, 4733. [f] The erythro/threo ratio of the β-siloxy aldehyde is 1:3 by ^{1}H NMR analysis. [g] Optically active (+)-*trans*-piperitol was kindly provided by the Takasago Co. Ltd. [h] The rearrangement was effected at −20 °C. [i] Optically active (+)-*cis*-piperitol was prepared from (+)-*trans*-piperitol by the Swern oxidation followed by reduction with DIBAH. [j] At 0 °C.

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(1) Reviews on the Lewis acid mediated rearrangement of epoxides: (a) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737. (b) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. See, also: Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 1693. Milstein, D.; Buchman, O.; Blum, J. *Tetrahedron Lett.* **1974**, 2257. For the transformation of 2,3-epoxy alcohols and their derivatives, see: Bahrens, C. H.; Sharpless, K. B. *Aldrich. Acta* **1983**, *16*, 67.

(2) (a) Hill, J. G.; Sharpless, K. B. *Org. Synth.* **1984**, *63*, 66. (b) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

(3) (a) Masamune, S.; Choy, W. *Aldrich. Acta* **1982**, *15*, 47. (b) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (c) Danishefsky, S. J. *Aldrich. Acta* **1986**, *19*, 59.

(4) Maruoka, K.; Hasegawa, M.; Yamamoto, H.; Suzuki, K.; Shimazaki, M.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1986**, *108*, 3827. See, also: Suzuki, K.; Miyazawa, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1987**, *28*, 3515. Shimazaki, M.; Hara, H.; Suzuki, K.; Tsuchihashi, G. *Tetrahedron Lett.* **1987**, *28*, 5891.

(5) For another type of the epoxy alcohol rearrangement with $Ti(O\text{-}i\text{-}Pr)_4$, see: Morgans, D. J.; Sharpless, K. B.; Traynor, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 462.

(6) Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 7922.

(7) $[\alpha]_D$ −19° (*c* 0.83, benzene) for (*S*)-isomer: Suzuki, K.; Kitayama, E.; Matsumoto, T.; Tsuchihashi, G. *Tetrahedron Lett.* **1984**, *25*, 828.

(8) Harada, T.; Hayashiya, T.; Wada, I.; Iwa-ake, N.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 527.

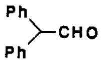
(9) The (*S*)-2-phenylpropanol ($[\alpha]_D$ −18.6° (*c* 0.84, benzene)) derived from **2** possesses virtually the same optical purity as the starting silyl ether **1**.

(10) The optical purity of **6** was substantiated by GLC analysis after converting to the acetal of (−)-2(*R*),4(*R*)-pentanediol.

tically active epoxy silyl ether, which was readily obtained by the enantioselective epoxidation of racemic (*E*)-4-phenyl-3-buten-2-ol,[11] was smoothly rearranged under the influence of the reagent A producing the optically active, *threo*-β-siloxy aldehyde **8** exclusively (entry 5).[12]

Other selected examples in Table I concerning the epoxy alcohol rearrangement clearly indicate the effectiveness of our approach. As a whole, the facile migration of the alkyl group was observed in the case of γ,γ-disubstituted epoxy alcohols (entries 3, 4, 7, and 8). The γ-monosubstituted epoxy alcohols possessing aryl or alkenyl groups are also susceptible toward the rearrangement (entries 1, 2, 5, and 6).[13] This rearrangement is not dependent on the configuration of the β-carbon as both epoxy geraniol and epoxy nerol gave rise to the same aldol **6** as a sole isolable product (entries 3 and 4). The superiority of the reagent A over related organoaluminum reagents as well as other Lewis acids was examined with the substrate **5**. Attempted use of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD)[14,15] significantly retarded the rate of the rearrangement, showing the importance of the *p*-bromo substituent in the reagent A for rate acceleration of the reaction. Less bulky dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide lowered the yield (63%) of the reaction, while methylaluminum bis(4-bromo-2,6-diisopropylphenoxide) afforded only trace of **6**.[16] Consequently, use of two bulky 4-bromo-2,6-di-*tert*-butylphenoxy ligands in the reagent A is crucial for effecting the smooth rearrangement. It should be noted that this transformation cannot be easily accomplished by using the conventional Lewis acids. Attempted reaction of the substrate **5** with $TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$, and $BF_3{\cdot}OEt_2$ gave none of the desired product **6**.[17]

The bulky aluminum reagent A is also applicable to the rearrangement of a variety of simple epoxides such as stilbene oxide, 1-phenylcyclohexene oxide, 2-methyl-1-undecene oxide, and the *tert*-butyldimethylsilyl ether of epoxy citronellol, providing the corresponding aldehydes **9–12** in 90–98% yields.[18]



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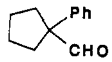

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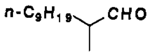

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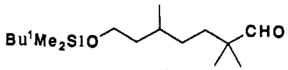

12

Supplementary Material Available: Experimental details and spectral data (^1H NMR, IR, $[\alpha]_D{}^{24}$, and elemental analysis) for all new compounds (7 pages). Ordering information is given on any current masthead page.

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[11] Martin, V. S.; Woodard, S. S.; Kastuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237.

[12] The stereostructural assignment of the aldol product **8** was determined by the correlation with the known methyl *threo*-3-hydroxy-2-phenylbutanoate (Mulzer, J.; Lammer, O. *Chem. Ber.* **1986**, *119*, 2178).

[13] Epoxy alcohols with other substitution patterns undergo no desired rearrangement. For example, the *tert*-butyldimethylsilyl ether of *trans*-2,3-epoxy-1-hexanol (γ-monosubstituted epoxy alcohol having alkyl groups) was unreactive with the reagent A after several hours at $-78 \sim -20$ °C and gradually decomposed at 0 °C. The *tert*-butyldimethylsilyl ether of (*E*)-2,3-epoxy-2-methyl-1-pentanol (β,β-disubstituted epoxy alcohol) gave 2-[(*tert*-butyldimethylsiloxy)methyl]-2-methylbutanal in 57% yield with migration of the ethyl group under the standard conditions.

[14] Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588.

[15] The rearrangement of **5** to **6** was over instantaneously with the reagent A at −78 °C, while MAD requires higher reaction temperature (−20 °C for several hours).

[16] The ring-opening product, 1-(*tert*-butyldimethylsiloxy)-3,7-dimethyl-3,6-octadien-2-ol was isolated in 16% yield as a major product.

[17] With the conventional Lewis acids the isolable products presumably follow: $BF_3{\cdot}OEt_2$: 1-(*tert*-butyldimethylsiloxy)-3,7-dimethyl-3-fluoro-6-octen-2-ol; $TiCl_4$: 2-(*tert*-butyldimethylsiloxy)-1-[2-(1-chloro-1-methylethyl)-1-methylcyclobutyl]ethanol. With $Ti(O\text{-}i\text{-}Pr)_4$, no rearrangement occurred, and the substrate **5** was recovered in more than 90% yield.

[18] Attempted rearrangement of *tert*-butyldimethylsilyl ether of epoxy citronellol with $BF_3{\cdot}OEt_2$ resulted in formation of a number of deteriorated reaction products.

Nickel-Catalyzed Intramolecular [4 + 2] Dienyne Cycloadditions: An Efficient New Method for the Synthesis of Polycycles Containing Cyclohexa-1,4-dienes

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Received March 21, 1989

The low reactivity of unactivated alkynes as dienophilic reagents has proven to be a major limitation of the Diels–Alder reaction.[1] In order to circumvent the forcing and often deleterious thermal conditions required for [4 + 2] cycloadditions involving such alkynes,[1] several imaginative alternatives employing alkyne equivalents have been developed.[2] Utilization of these equivalents in formal dienyne cycloadditions normally requires pre- and post-cyclization substrate modifications, thereby representing only an indirect solution to this reactivity dilemma. As an alternative to the use of alkyne equivalents, titanium-,[3] iron-,[4] and rhodium-[5]mediated intermolecular dienyne cycloadditions have been examined. Although the application of these catalysts to intramolecular cycloadditions has not been investigated, these direct approaches have been limited by product aromatization or isomerization, competing oligomerizations, modest yields, extended reaction times, and/or a lack of established generality. The capability of nickel(0) to catalyze C–C bond formation between two dienes[6] and the advantages of this process in complex molecule total synthesis[7] prompted our examination of nickel catalysts for dienyne cycloadditions. This investigation has led to the development of the first nickel(0) catalyst system which provides a practical, direct, and mild dienyne cycloaddition approach to 1,4-cyclohexadiene-containing polycycles.

Illustrative of the efficacy of this method, *treatment of the sorbic acid derived dienyne* ***1***[8] (Table I) *with 10 mol % Ni(COD)$_2$ and*

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[1] This limitation was initially treated by Sauer (Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 211) and is reinforced in recent reviews on the Diels–Alder reaction: Ciganik, E. *Org. React.* **1984**, *32*, 1. Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. Taber, D. F. *Intramolecular Diels–Alder and Ene Reactions*; Springer-Verlag: Berlin, 1984. Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. The problems attending thermal dienyne cycloadditions have limited the number of examples of this process in synthesis. For some recent examples which provide calibration on the thermal requirements for such reactions, see: (a) Shea, K. J.; Burke, L. D. *J. Org. Chem.* **1988**, *53*, 318. (b) Kanematsu, K.; Hayakawa, K.; Yodo, M.; Ohsuki, S. *J. Am. Chem. Soc.* **1984**, *106*, 6735. (c) Liu Z.-Y.; Zhou, X.-R.; Wu, Z.-M. *J. Chem. Soc., Chem. Commun.* **1987**, 1868. (d) Cyclization involving a deca-7,9-dien-1-yne was found to require 150 °C, 72 h, 89% (Trost, B. M. Stanford University, personal communication, 1988). (e) Cyclizations involving nona-6,8-dien-1-ynes were found to require 150 °C, 5 h, 65–68% (Roush, W. R. Indiana University, personal communication, 1988).

[2] For a general review, see: (a) De Lucchi, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585. Recent examples of acetylene or general alkyne equivalents include the following: (trimethylsilyl)vinyl sulfone (Carr, R. C. V.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853), ethynyl sulfone (Davis, A. P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639), vinyl sulfoxide (Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597), (*E*)- or (*Z*)-1,2-bis(phenylsulfonyl)ethylene (De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596), maleic anhydride (Westberg, H. H.; Dauben, H. J. *Tetrahedron Lett.* **1968**, 5123) and 1,4-benzodithiin-1,1,4,4-tetraoxide (Nakayama, J.; Nakamura, Y.; Hoshino, M. *Heterocycles* **1985**, *23*, 1119).

[3] Mach, K.; Antropiusova, H.; Petrusova, L.; Turecek, F.; Hanus, V. *J. Organomet. Chem.* **1985**, *289*, 331.

[4] (a) tom Dieck, H.; Diercks, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 778; *Angew. Chem. Suppl.* **1983**, 1138. (b) Carbonaro, A.; Greco, A.; Dall'Asta, G. *J. Org. Chem.* **1968**, *33*, 3948. (c) Genet, J. P.; Ficini, J. *Tetrahedron Lett.* **1979**, *17*, 1499.

[5] Matsuda, I.; Shibata, M.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1987**, *28*, 3361.

[6] For reviews and lead references, see: (a) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185. (b) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, pp 613–797. (c) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1975; Vol. 2. (d) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. (e) Wender, P. A.; Snapper, M. L. *Tetrahedron Lett.* **1987**, *28*, 2221. (f) Dienyne cyclizations are being investigated by Professor Y. Ito and co-workers and will be reported in due course (Ito, Y., personal communication, May 1989).

[7] Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1988**, *110*, 5904.

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