into a single enantiomer has been reported,[11] the practical application to an important and chemically complex intermediate (*RS*)-**3** has rarely been achieved. The simplicity and efficiency of this asymmetric transformation make it the clear method of choice in this case. Although such methods are not currently in vogue, their utility should not be overlooked.

Acknowledgment. We are deeply indebted to T. Truppi, Dr. A. O. King, and Dr. J. M. McNamara for their support. We are also grateful to Drs. Roger Freidinger and Mark G. Bock for many helpful discussions and procedures.

(14) **Physical Data. 2** (L-364,718): $[\alpha]^{25}_D$ -113.7° (*c* 1, CH_3CN); IR (KBr) 3400, 3280, 1695, 1647, 1540, 1510, 1491 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.53 (s, 3 H, CH_3N), 5.76 (d, 1 H, *J* = 8 Hz, CHN), 7.1-7.7 (m, 14 H, Ar), 8.07 (d, 1 H, *J* = 8 Hz, NH), 9.4 (s, 1 H, indole NH). Anal. Calcd for $C_{25}H_{20}N_4O_2$: C, 73.51; H, 4.94; N, 13.72. Found: C, 73.22; H, 5.01; N, 13.52. (*RS*)-**3** (free base): mp 110-112 °C; IR (KBr) 3378, 3310, 1675, 1605 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.4 (br, 2 H, NH_2), 3.47 (s, 3 H, CH_3N), 4.47 (s, 1 H, $CHNH_2$), 7.18-7.64 (m, 9 H, Ar). (*RS*)-**3** (benzenesulfonic acid salt): mp 224-227 °C. Anal. Calcd for $C_{22}H_{21}N_3O_4S$: C, 62.40; H, 5.00; N, 9.92; S, 7.57. Found: C, 62.09; H, 4.88; N, 10.07; S, 7.67. (*S*)-**3** (free base): mp 148-149 °C; $[\alpha]^{25}_D$ -269° (*c* 1, CH_3CN). (*S*)-**3** (CSA salt): mp 135-138 °C; $[\alpha]^{25}_D$ -27.8° (*c* 1, H_2O); NMR (CD_3CN, 300 MHz) δ 3.52 (s, 3 H, CH_3N), 5.24 (s, 1 H, $CHNH_3^+$). Anal. Calcd for $C_{26}H_{31}N_3O_5S \cdot 0.75H_2O$: C, 61.09; H, 6.41; N, 8.22; S, 6.27. Found: C, 60.96; H, 6.25; N, 8.59; S, 6.18. (*RS*)-**5**: mp 178-180 °C; NMR ($CDCl_3$, 300 MHz) δ 1.6 (s, 1 H, ArOH), 3.48 (s, 3 H, CH_3N), 5.5 (s, 1 H, CHN=C), 7.23-7.75 (m, 11 H, Ar), 9.24 (s, 1 H, N=CH). Anal. Calcd for $C_{23}H_{17}Cl_2N_3O_2$: C, 63.02; H, 3.91; N, 9.59; Cl, 16.18. Found: C, 63.02; H, 4.19; N, 9.66; Cl, 15.95.

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Metalated Allylaminosilane: A New, Practical Reagent for the Stereoselective α-Hydroxyallylation of Aldehydes to Erythro-1,2-diol Skeletons[1]

Summary: A zinc reagent derived from allyl(diisopropylamino)dimethylsilane reacts with aldehydes regio- and stereoselectively to form *erythro*-3-silyl-1-alken-4-ols, which are further transformed into *erythro*-1-alkene-3,4-diols by hydrogen peroxide oxidation of the carbon-silicon bonds.

Sir: Much effort has been devoted to the stereocontrolled synthesis of erythro and threo[2] 1,2-diols in connection with the total synthesis of a variety of polyoxy natural products. The existing methodologies include (1) dihydroxylation[3] or epoxidation[4] of stereodefined olefins, (2) reduction[5] or alkylation[6] of α-hydroxy carbonyl compounds, and (3) reaction of the carbonyl group with α-hydroxy carbanions or their equivalents.[7] The last method is quite unique and attractive, since the carbon-carbon bond formation and the stereocontrolled generation of two chiral centers on both sides of the substrate and the reagent may be achieved simultaneously. Several types of metalated allyl ethers have been successfully used.[7] Since intramolecular chelation between oxygen and metal in such reagents fixes the *Z* configuration,[7,8] threo isomers are created rather readily with boron or aluminum reagents through six-membered transition states, as exemplified by A.[7a-c] On the other hand, erythro isomers are relatively inaccessible[7c,j] owing to the lack of availability of *E* isomers. A facile route to erythro 1,2-diols would complement existing methodology.

We have recently devised a novel, practical route to erythro isomers. Our method uses the zinc reagent **2** derived from an allylaminosilane **1** as an α-hydroxyallyl anion equivalent, as shown in Scheme I. The absence of intramolecular chelation by nitrogen on silicon has been suggested by formation of (*E*)-$(R_2N)Me_2SiCH{=}CHCH_2SiMe_3$ exclusively upon quenching the metalated species with Me_3SiCl. Thus, our predicted stereochemical outcome through the most favorable cyclic transition state (B)[9] should be erythro. In addition to the complete stereocontrol, the exclusive α-regioselectivity observed with aldehydes is noted, since the zinc reagent **2** reacted with ketones exclusively γ to silicon.[10] The presence of the bulky (*i*-$Pr_2N)Me_2Si$ group in the zinc reagent was essential for our new process: otherwise formation of 1,3-dienes arising from the Peterson olefination predominated under the alkylation conditions.

In a general procedure, allyl(diisopropylamino)dimethylsilane (**1**)[11] was lithiated with *n*-BuLi (a hexane solution, 1 equiv) in the presence of TMEDA (1 equiv) in Et_2O at 0 °C for 4 h. The resulting solution was added to dried $ZnCl_2$ (1 equiv) at 0 °C. After being stirred at 0 °C for 1 h, the white suspension was cooled to -78 °C followed by the dropwise addition of aldehyde (0.7 equiv). The mixture was allowed to warm to 0 °C cover 2 h and stirred for another 2 h.[12] After evaporation of the volatile materials in vacuo, the remaining solids were subjected to oxidative cleavage of the carbon-silicon bond [30% H_2O_2 (20 molar equiv)/KF (2 equiv)/$KHCO_3$ (2 equiv)/MeOH/THF/room temperature/5-15 h][13] and the usual

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(11) Prepared in two steps from Me_2SiCl_2 by (1) monoamination [*i*-Pr_2NH, 3 equiv, 80 °C; 81% yield; bp 94-96 °C (48 mmHg)] and (2) allylation [$CH_2{=}CHCH_2MgCl$, Et_2O; 85% yield; bp 86-88 °C (18 mmHg)].

(12) It was also possible to isolate the intermediate adduct at this stage as an O-silylated form **3** by treatment with Me_3SiCl (2 equiv) at 0 °C to room temperature overnight. Yields are listed in Table I.

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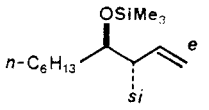
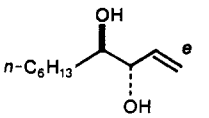
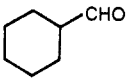
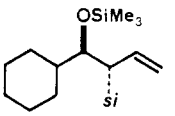
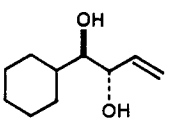
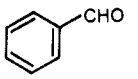
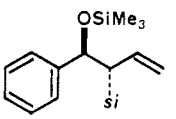
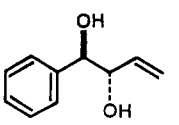
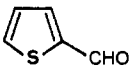
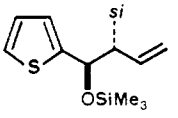
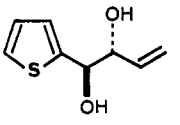
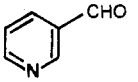
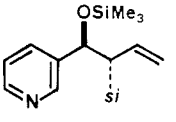
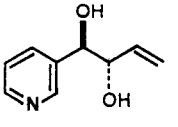
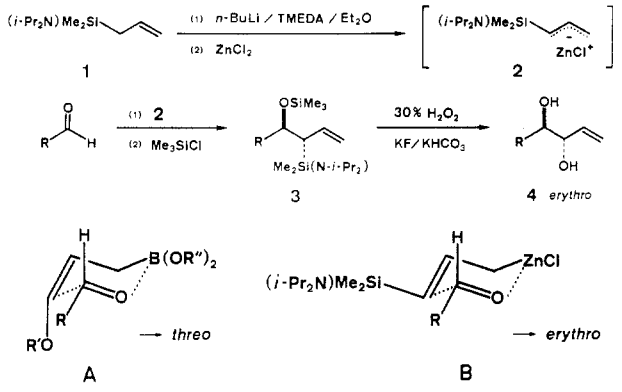
Table I. Stereoselective α-Silylallylation and α-Hydroxyallylation of Aldehydes by 1[a]

entry	aldehyde	3[b,c]	yield, %	4[c]	yield,[d] %
1	n-$C_6H_{13}CHO$		53		78
2			54		61
3			97		80
4			87		72[f]
5			75		93

[a] All reactions were carried out on a 2-mmol scale according to the general procedure. Yields are for isolated pure products based on aldehyde. [b] si = $SiMe_2(N\text{-}i\text{-}Pr_2)$. [c] Products are all racemic. [d] Overall yields of diol obtained without isolation of 3. [e] A mixture of diastereoisomers in the ratio of ca. 4:1. [f] Yield from 3.

Scheme I



nonaqueous workup[14] followed by chromatography gave erythro-1-alkene-3,4-diols (4) in high yields.[15]

Representative results are summarized in Table I. Excepting a rather low stereoselectivity encountered with a linear alkanal (entry 1), erythro-1,2-diol skeletons have been constructed exclusively with α-branched alkyl, aromatic, and heteroaromatic aldehydes (entries 2–5).

α-Chiral aldehydes, such as isopropylideneglyceraldehyde, also gave the desired polyols highly stereoselectively under the standard conditions, as exemplified by eq 1, but in rather low overall yields.[16] Since in these cases 1,3-dienes and γ-regio isomers were formed as byproducts in comparable yields, further refinement is now under investigation.

The metalated allylsilanes have so far been studied only with allyltrimethylsilane or triphenylsilane mostly for the purpose of the stereoselective synthesis of (*E*)- and (*Z*)-1,3-dienes.[9,10,17] We have now demonstrated that a silafunctional allylsilane serves in an unprecedented manner as an α-hydroxyallyl anion equivalent. Since allylaminosilane 1 is readily available and is stable enough to usual handling, the present procedure may provide the most facile and practical approach to construction of erythro-1,2-diol skeletons from aldehydes.

5 6, 28% yield (1)

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(16) The corresponding acetonide of **6** was found to be isomerically pure by the 400-MHz NMR and GLC analysis; the 2,3-erythro stereochemistry was tentatively assigned in view of the known stereochemical course the action of organozinc reagents to the glyceraldehyde. Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447. Mulzer, J.; Angermann, A. *Tetrahedron Lett.* **1983**, *24*, 2843. Suzuki, K.; Yuki, Y.; Mukaiyama, T. *Chem. Lett.* **1981**, 1529.

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