the corresponding epoxide.[24] ***cis*-1-Cyclohexyl-1,2-epoxyoctane.** ^{1}H NMR ($CDCl_3$): δ 0.81 (t, J = 6.9 Hz, 3 H), 0.9–1.5 (m, 12 H), 1.3–1.6 (m, 4 H), 1.4–1.8 (m, 4 H), 1.8–2.0 (m, 1 H), 2.55 (dd, J = 4.0, 8.0 Hz, 1 H), 2.8–2.9 (m, 1 H).

(*Z*)-2,2-Dimethyl-3-undecene. Bp: 88–90 °C (bath temperature, 13 Torr). IR (neat): 2954, 2922, 1729, 1466, 1363, 1273 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.7 Hz, 3 H), 1.08 (s, 9 H), 1.1–1.5 (m, 10 H), 2.0–2.3 (m, 2 H), 5.15 (dt, J = 12.0, 7.0 Hz, 1 H), 5.31 (d, J = 12.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.4, 29.3, 29.4, 30.4, 31.2, 31.9, 33.1, 129.1, 139.6. MS: m/z (rel intensity) 182 (M^+, 3), 139 (3), 97 (20), 83 (100), 69 (69), 55 (48). Anal. Calcd for $C_{13}H_{26}$: C, 85.63, H, 14.37. Found: C, 85.61; H, 14.54. The E/Z ratio was determined by ^{1}H NMR analysis of the corresponding epoxide.[24] ***cis*-2,2-Dimethyl-3,4-epoxyundecane.** ^{1}H NMR ($CDCl_3$): δ 0.87 (t, J = 6.8 Hz, 3 H), 0.98 (s, 9 H), 1.2–1.5 (m, 10 H), 1.6–1.9 (m, 2 H), 2.63 (d, J = 4.2 Hz, 1 H), 2.8–2.9 (m, 1 H). **(*E*)-2,2-Dimethyl-3-undecene.** ^{1}H NMR ($CDCl_3$): δ 0.92 (t, J = 6.7 Hz, 3 H), 0.99 (s, 9 H), 1.2–1.5 (m, 10 H), 1.9–2.1 (m, 2 H), 5.29 (dt, J = 15.7, 6.3 Hz, 1 H), 5.43 (d, J = 15.7 Hz, 1 H). ***trans*-2,2-Dimethyl-3,4-epoxyundecane.** ^{1}H NMR ($CDCl_3$): δ 0.81 (t, J = 6.8 Hz, 3 H), 0.85 (s, 9 H), 1.1–1.5 (m, 10 H), 1.5–1.6 (m, 2 H), 2.45 (d, J = 2.3 Hz, 1 H), 2.7–2.8 (m, 1 H).

(*Z*)-1-(Trimethylsilyl)-1-dodecene. Bp: 76–78 °C (bath temperature, 1 Torr). IR (neat): 2922, 2852, 1607, 1466, 1248, 837, 761, 688 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 9 H), 0.93 (t, J = 6.8 Hz, 3 H), 1.1–1.5 (m, 16 H), 2.0–2.2 (m, 2 H), 5.45 (d, J = 14.0 Hz, 1 H), 6.29 (dt, J = 14.0, 7.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 0.58, 14.1, 22.7, 29.4, 29.8, 32.0, 33.6, 128.7, 149.3. MS: m/z (rel intensity) 240 (M^+, 0.8), 225 (50), 114 (27), 73 (100), 59 (61). Anal. Calcd for $C_{15}H_{32}Si$: C, 74.91; H, 13.41. Found: C, 74.48; H, 13.57. The E/Z ratio was determined by ^{1}H NMR analysis. **(*E*)-1-(Trimethylsilyl)-1-dodecene.** ^{1}H NMR ($CDCl_3$): δ 0.02 (s, 9 H), 0.85 (t, J = 6.7 Hz, 3 H), 1.1–1.5 (m, 16 H), 2.0–2.2 (m, 2 H), 5.59 (d, J = 18.0 Hz, 1 H), 6.02 (dt, J = 18.0, 6.1 Hz, 1 H).

(*Z*)-1,6-Undecadiene.[25] ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J = 7.0 Hz, 3 H), 1.2–1.4 (m, 4 H), 1.46 (dd, J = 6.9, 7.3 Hz, 2 H), 1.9–2.2 (m, 6 H), 4.95 (d, J = 10.3 Hz, 1 H), 5.01 (d, J = 17.0 Hz, 1 H), 5.3–5.5 (m, 2 H), 5.82 (ddt, J = 10.3, 17.0, 6.8 Hz, 1 H). The E/Z ratio was determined by ^{1}H NMR analysis of the corresponding epoxide.[24] ***cis*-6,7-Epoxy-1-undecene.** ^{1}H NMR ($CDCl_3$): δ 0.93 (t, J = 6.8 Hz, 3 H), 1.2–1.8 (m, 10 H), 2.0–2.3 (m, 2 H), 2.9–3.0 (m, 2 H), 4.98 (d, J = 17.1 Hz, 1 H), 5.01 (d, J = 10.3 Hz, 1 H), 5.82 (ddt, J = 10.3, 17.1, 6.6 Hz, 1 H).

(*Z*)-1,7-Octadecadiene. Bp: 103–105 °C (bath temperature, 0.20 Torr). IR (neat): 2922, 2852, 1735, 1642, 1460, 1271, 991 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3 H), 1.2–1.5 (m, 16 H), 1.3–1.5 (m, 4 H), 1.9–2.2 (m, 6 H), 4.95 (d, J = 10.3 Hz, 1 H), 5.00 (d, J = 16.9 Hz, 1 H), 5.3–5.5 (m, 2 H), 5.82 (ddt, J = 10.3, 16.9, 6.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 27.0, 27.2, 28.6, 29.2, 29.4, 29.6, 29.7, 29.8, 31.9, 33.7, 114.2, 129.6, 130.1, 139.0. MS: m/z (rel intensity) 250 (M^+, 4), 123 (9), 96 (75), 82 (100), 67 (76), 55 (79). Anal. Calcd for $C_{18}H_{34}$: C, 86.32; H, 13.68. Found: C, 86.18; H, 13.61. The E/Z ratio was determined by ^{1}H NMR analysis of the corresponding epoxide.[24] ***cis*-7,8-Epoxy-1-octadecene.** ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.2–1.5 (m, 14 H), 1.3–1.6 (m, 10 H), 2.0–2.1 (m, 2 H), 2.9–3.0 (m, 2 H), 4.95 (d, J = 10.2 Hz, 1 H), 5.01 (d, J = 17.1 Hz, 1 H), 5.81 (ddt, J = 10.2, 17.1, 6.6 Hz, 1 H).

(*Z*)-5-Octadecen-1-ol. Bp: 146–147 °C (bath temperature, 0.30 Torr). IR (neat): 3318, 2922, 2850, 1652, 1466, 1067 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.1–1.5 (m, 21 H), 1.4–1.5 (m, 2 H), 1.5–1.7 (m, 2 H), 1.9–2.2 (m, 4 H), 3.6–3.7 (m, 2 H), 5.3–5.5 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.2, 22.7, 25.9, 26.9, 27.3, 29.4, 29.6, 29.7, 31.9, 32.4, 62.9, 129.3, 130.4. MS: m/z (rel intensity) 250 ($M^+ - H_2O$, 6), 123 (10) 96 (58), 82 (100), 41 (66). Anal. Calcd for $C_{18}H_{36}O$: C, 80.53; H, 13.52. Found: C, 80.56; H, 13.63. The E/Z ratio was determined by ^{1}H NMR analysis of the epoxide[24] of the *tert*-butyldimethylsilyl ether of the alcohol. ***cis*-5,6-Epoxy-1-(*tert*-butyldimethylsiloxy)octadecane.** ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 6 H), 0.86 (s, 12 H), 1.2–1.4 (m, 16 H), 1.4–1.8 (m, 12 H), 2.9–3.0 (m, 2 H), 3.62 (t, J = 5.9 Hz, 2 H).

Registry No. **1**, 765-03-7; **2**-d_2, 127863-12-1; **3a**, 87969-78-6; **3b**, 138384-24-4; **4**, 125641-95-4; **5**, 121134-52-9; **6**, 6975-99-1; **6**-d_2, 125642-23-1; phenylacetylene, 536-74-3; cyclodecyne, 3022-41-1; 1-phenyl-1-octyne, 16967-02-5; 1-cyclohexyl-1-octyne, 125641-94-3; (*Z*)-6-dodecene, 7206-29-3; (*Z*)-cyclododecene, 1129-89-1; (*Z*)-1-phenyl-1-octene, 42036-72-6; (*Z*)-1-cyclohexyl-1-octene, 62444-54-6; *cis*-1-cyclohexyl-1,2-epoxyoctane, 106262-67-3; *cis*-2,2-dimethyl-3,4-epoxyundecane, 138813-13-5; *trans*-2,2-dimethyl-3,4-epoxyundecane, 138813-14-6; (*Z*)-2,2-dimethyl-3-undecene, 125642-19-5; (*Z*)-1-(trimethylsilyl)-1-dodecene, 70875-30-8; (*E*)-1-cyclohexyl-1-octene, 87393-89-3; (*E*)-2,2-dimethyl-3-undecene, 14033-68-2; (*E*)-1-(trimethylsilyl)-1-dodecene, 70875-31-9; (*Z*)-1,6-undecadiene, 91914-03-3; *cis*-6,7-epoxy-1-undecane, 138813-17-9; (*Z*)-1,7-octadecadiene, 127863-11-0; *cis*-7,8-epoxy-1-octadecene, 138813-15-7; (*Z*)-5-octadecen-1-ol, 41207-39-0; *cis*-5,6-epoxy-1-(*tert*-butyldimethylsiloxy)octadecane, 138813-16-8; 1-undecen-6-yne, 127863-09-6; 1-octadecen-7-yne, 127863-10-9; 5-hexadecyn-1-ol, 72443-47-1; (*Z*)-5-hexadecen-1-ol, 106463-48-3; niobium chloride, 10026-12-7; zinc, 7440-66-6; tantalum chloride, 7721-01-9; 1-dodecene, 112-41-4; styrene, 100-42-5.

Supplementary Material Available: Spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS) for internal alkynes and two experimental procedures (5 pages). Ordering information is given on any current masthead page.

(24) Epoxidation was conducted with mCPBA in CH_2Cl_2 at 0 °C. The following procedure was modified. Paquette, L. A.; Barrett, J. H. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 467.

(25) Barluenga, J.; Yus, M.; Concellon, J. M.; Bernad, P.; Alvarez, F. *J. Chem. Res. (S)* **1984**, 122.

High Regioselectivity in the Alternative, Reductive Cleavages of Terminal Epoxides with Aluminum Reagents[1]

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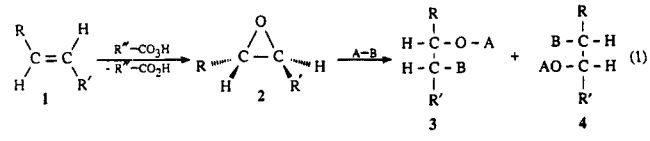
Introduction

One of the potentially most versatile methods for functionalizing a carbon skeleton is the Prilezhaev epoxidation of a carbon–carbon double bond (1)[2] and the ring opening of the oxirane **2** by a polar reagent, A–B (eq 1):[3]



(1)

With an unsymmetrical alkene, even if the ring opening were to occur in a stereospecific, S_N2 manner (e.g., **3** and **4**), there remains the further complication of a nonregioselective ring opening leading to various proportions of regioisomers **3** and **4**. A significant improvement in the utility and versatility of this method for organic synthesis would be the discovery of A–B reagents and experimental conditions that cleave oxiranes in a highly regioselective manner and thereby lead either to product **3** or to product **4** in high yield.

For this study, we have chosen oxiranes derived from terminal olefins as our test substrates because functionality at or near the end of a carbon chain is often the most valuable site for carbon–carbon chain elongation. As a potentially valuable cleavage process, we have selected reduction with sources of aluminum hydride.

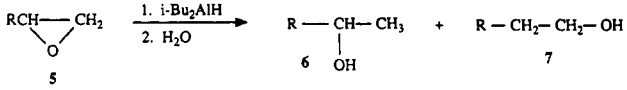
(1) Part 48 of the series *Organometallic Compounds of Group III*. Part 47: Eisch, J. J.; Caldwell, K. R.; Werner, S.; Krüger, C. *Organometallics* **1991**, *10*, 3417.

(2) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin: New York, 1965; pp 109–123.

(3) Parker, R. E.; Isaac, N. S. *Chem. Rev.* **1959**, *59*, 737.

0022-3263/92/1957-1618$03.00/0

Table I. Relative Cleavage of Terminal Epoxides with Neutral Organoaluminum Reagents[a]



5 6 7

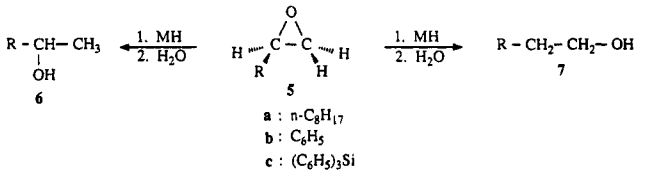
epoxide [b] (R)	entry	reagent	solvent[b]	temp (°C) (time (h))	yield (%)	ratio 6:7
n-octyl	1	i-Bu_2AlH i-Bu_2Al-O-s-Bu	n-C_7H_{16}	25 (8)	95	100:0
	2	i-Bu_2AlH	n-C_7H_{16} *N*-methylpyrrolidine[c]	50 (20)	85	99:1
	3	i-Bu_2AlH	n-C_7H_{16}	100 (20)	91	96:4
	4	i-Bu_3Al	n-C_7H_{16}	100 (24)	55	55:45[d]
	5	i-Bu_3Al	Et_2O	35 (30)	60	23:77
	6	i-Bu_3Al	THF	60 (6)	93	0:100
phenyl	7	i-Bu_3Al	n-C_7H_{16}	100 (2)	35	0:100[d]
	8	i-Bu_3Al	THF	25 (10)	85	7:93
	9	i-Bu_2AlH i-Bu_2Al-O-s-Bu	n-C_7H_{16}	25 (20)	95	14:86
	10	i-Bu_3Al Et_3N[c]	n-C_6H_{14}	25 (12)	90	18:82
	11	i-Bu_2AlH	n-C_7H_{16}	80 (10)	96	32:68
	12	i-Bu_2AlH	nC_7H_{16} *N*-methylpyrrolidine[c]	25 (12)	85	65:35
	13	$LiAlH_4$	THF	25 (1)	95	97:3[e]
triphenylsilyl	14	i-Bu_3Al	THF	25 (18)	75[f]	65:35
	15	i-Bu_3Al	n-C_6H_{14}	25 (18)	90[f]	60:40
	16	i-Bu_2AlH	n-C_6H_{14}	25 (1)	90	0:100
	17	i-Bu_3Al	n-C_6H_{14} Et_3N[c]	25 (18)	0[g]	

[a] The reagents were stirred in the stated medium at the indicated temperature and for the given time. The cooled solution was cautiously treated dropwise with water (*gas evolution*!) and then with 1 N aqueous HCl. The product was extracted into diethyl ether, the ether extracts were dried over anhydrous $MgSO_4$, and the volatiles were evaporated. The reaction product mixture was analyzed or separated by gas chromatography or flash column chromatography. [b] The reagents, either commercially available (i-Bu_2AlH and i-Bu_3Al (Texas Alkyls) or generated in situ i-Bu_2Al-O-s-Bu from i-Bu_2AlH and s-BuOH), were employed in 10% excess. [c] The tertiary amine employed was equimolar with the aluminum reagent. [d] The action of i-Bu_3Al on epoxide **5a** or **5b**, when conducted in hydrocarbon solution, led to considerable amounts of RCH(i-Bu)CH_2OH (cf. ref 13) but the use of donor solvents suppressed such isobutylated products and gave excellent regioselectivity for the primary alcohol **7** (Cf. runs 6 and 8). [e] This highly regioselective conversion to 1-phenylethanol by $LiAlH_4$ in THF, reproduced in this work, was already observed by Yoon and Brown (*J. Am. Chem. Soc.* **1968**, *90*, 2927). [f] The balance of the completely consumed epoxide was found as triphenylvinylsilane (25% in entry 14, 10% in entry 15). This olefin probably results from a metalation of the epoxide carbon α to the silicon and a carbenoid α elimination.[14] [g] The epoxide was consumed but no alcohol was isolated. The principal products were triphenylvinylsilane (cf. footnote f), Ph_3SiOH, and $Ph_2SiOCH{=}CH_2$. The latter two products undoubtedly stem from a base-promoted isomerization of the epoxide (cf. ref 15).

The reductive cleavage of terminal epoxides has been examined previously in studies that have variously employed $LiAlH_4$ in ether,[4,5] $LiAlH_4$–$AlCl_3$,[4,6] AlH_3–$AlCl_3$,[5] $LiBH_4$–MeOH,[7] $NaBH_3CN$,[8] $NaAlH_2(OR)_2$,[9] $NaBH_4$,[10] $LiBH_4$–$Ti(OR)_4$,[11] n-Bu_3SnH–NaI,[12] and i-Bu_3Al.[13] Some high regioselectivities were observed in these investigations but no type of reagent was capable of yielding both the primary or the secondary alcohol in high regioselectivity by a simple modification of experimental conditions. Moreover, most such reductions were conducted in ethereal solution whose Lewis basic character might influence the reactivity of the hydride source.

To explore the influence of the one substituent on the regiochemistry of terminal epoxide ring cleavages, we have examined the reduction of alkyl-, aryl-, and silyl-substituted epoxides, namely 1,2-epoxydecane (**5a**), styrene oxide (**5b**), and (epoxyethyl)triphenylsilane (**5c**), by such neutral hydride sources as i-Bu_2AlH and i-Bu_3Al. Although these

Scheme I



reagents would also form etherate complexes when employed in etheral media,[14] they are freely soluble in hydrocarbons without complexation.[15,16] Thus, we have been

(4) (a) Eliel, E. L.; Delmonte, D. W. *J. Am. Chem. Soc.* **1958**, *80*, 1744. (b) Eliel, E. L.; Rerick, M. N. *J. Am. Chem. Soc.* **1960**, *82*, 1362.
(5) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927.
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(11) Dai, L.-X.; Lou, B.-L.; Zhang, Y.-Z.; Guo, G.-Z. *Tetrahedron Lett.* **1986**, *27*, 4343.
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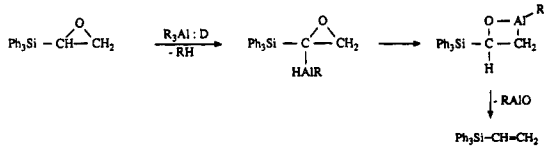
(13) Namy, J.-L.; Abenhaim, D. *J. Organomet. Chem.* **1972**, *43*, 95.

(14) The varying amounts of triphenyl(vinyl)silane formed in these reactions (entries 13 and 14, 10–25%) probably stem from metalization of the epoxide carbon α to silicon and an α-elimination process: Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293.



(15) Rearrangements of α,β-epoxyalkylsilanes have been previously reported: Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1976**, *41*, 2615.
(16) Eisch, J. J.; Chiu, C. S. *J. Organomet. Chem.* **1988**, *358*, C1. Aluminum halides can cleave epoxides, often with the initiation of carbenium ion rearrangements leading to carbonyl or skeletal isomers. For this reason, we had wished to avoid using combinations of $LiAlH_4$ or i-Bu_2AlH with $AlCl_3$ to achieve regioselective reductions of epoxides. However, this procedure has been employed with considerable success by Eliel and co-workers; cf. Eliel, E. L.; Rerick, M. N. *J. Am. Chem. Soc.* **1960**, *82*, 1362.

able to vary systematically both the solvent and the Lewis base (R_2O or R_3N) employed in such epoxide reductions. As a result, we have now observed that the regiochemistry of these reductive cleavages can be advantageously steered by a rational choice of experimental conditions.

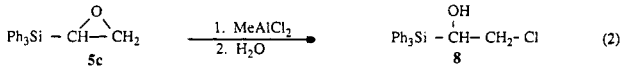
Results

By the reaction of either i-Bu_2AlH or i-Bu_3Al with terminal epoxides **5a–5c**, in the presence or the absence of Lewis bases such as ethers or amines, a highly regioselective cleavage into either the primary alcohol **7** or the secondary alcohol **6** (Scheme I) was observed (Table I). With the alkyl- and aryl-substituted epoxides **5a** and **5b**, it was found that the use of i-Bu_2AlH, specifically in the presence of a Lewis base (R_3N, R_2AlOR', R_2O), favors the formation of the secondary alcohol **6**. Indeed, a comparison of entries 1 and 4 shows that the regioselectivity can be made exclusive. On the other hand, the action of i-Bu_3Al, especially in the presence of a donor such as THF, favors the formation of the primary alcohol **7**. Again, such regioselectivity can become nearly exclusive, as reflected in entries 6 and 8. The use of a donor solvent with i-Bu_3Al also serves to sharply reduce the amount of isobutylation that accompanies reductive ring cleavage in hydrocarbon media.[13]

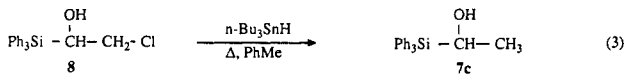
Although essentially exclusive regioselectivity leading to either **6** or **7** was attained with the alkyl-substituted epoxide **5a** (entries 1 and 6), the regioselectivity in reducing the aryl-substituted epoxide **5b** was not completely steerable. The primary alcohol could indeed be formed exclusively with i-Bu_3Al (entry 7), but the secondary alcohol could only be obtained in a 65% regioselectivity from the action of i-Bu_2AlH complexed with *N*-methylpyrrolidine (entry 12). However, the solution to this problem of obtaining **7** with high regioselectivity was already available: Yoon and Brown had shown that $LiAlH_4$ reduces **5c** to **6** in a 98% regioselectivity.[5] Their finding is reproduced in this study (entry 13).

The regioselectivities observed with the silyl-substituted epoxide **5c** ran counter to those found with the alkyl- and aryl-substituted epoxides **5a** and **5b**. The action of i-Bu_2AlH in the absence of any donor led exclusively to the primary alcohol (entry 16), while the action of i-Bu_3Al in THF led to the formation of the secondary alcohol in a 65% regioselectivity (entry 14). This regioselective formation of the secondary alcohol could not be improved; when a stronger Lewis was employed (Et_3N, entry 17), the epoxide apparently was consumed by a combination of metalation[14] and base-promoted isomerization[15] processes that led to the observed products vinyltriphenylsilane, triphenylsilane, and (vinyloxy)triphenylsilane.

The challenge of converting (epoxyethyl)triphenylsilane (**5c**) into the secondary alcohol with high selectivity had to be met, therefore, in another manner. Noting our recent finding that treatment of **5c** with $MeAlCl_2$ and then H_2O produces exclusively **8** in >90% yield (eq 2),[16] we were



(2)



(3)

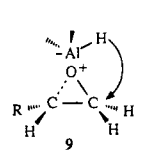
encouraged to seek a means of reductively dehalogenating **8** to produce **7c** (eq 3). Indeed, we have found that n-Bu_3SnH in toluene smoothly reduces **8** to **7c** in an isolated yield of 81%. Therefore, eqs 2 and 3 depict a high-yielding, two-step process for the exclusive regioselective conversion of **5c** into its secondary alcohol.

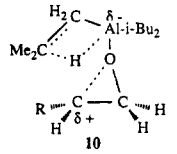
Thus, by judicious use of the appropriate aluminum reagent all three types of epoxides **5a–5c** can be transformed into either the corresponding primary alcohol or secondary alcohol in high yield and with great regioselectivity.

Discussion

Examination of the organoaluminum hydride reducing agents employed and the attendant experimental conditions (Table I) permits certain generalizations concerning the resultant dominant regioselectivity: (1) with the alkyl-substituted epoxides, the use of i-Bu_2AlH, without (entry 2) or with (entries 1 and 3) strong donors, favors the formation of the secondary alcohol, while the use of i-Bu_3Al favors the formation of the primary alcohol only with a strong donor (THF, entry 5); (2) with the phenyl-substituted epoxide, the use of i-Bu_3Al, with or without strong donors, always favors the formation of the primary alcohol, while the use of an aluminum hydride source favors the secondary alcohol only with the strongest donors (R_3N with i-Bu_2AlH in entry 12 and H^- with $LiAlH_4$ in entry 13); and (3) with the silyl-substituted epoxide, i-Bu_2AlH favors the primary alcohol and i-Bu_3Al favors the secondary alcohol.

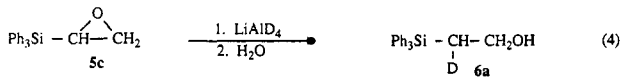
These empirical observations can be interpreted to mean that i-Bu_2AlH, which is actually present as a trimer in hydrocarbon media[17] but as a Lewis complex of the monomer in donor media, acts as a nucleophilic hydride source whose site of attack is governed by steric factors (**9**). With i-Bu_3Al, complexation with the epoxide prob-





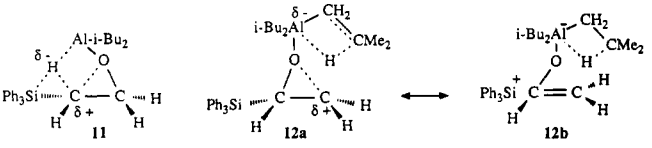
ably precedes isobutene elimination and the generation of the Al–H bond. The transition state for ring opening may be attained only with considerable stretching of a C–O bond and the development of carbenium-ion character (**10**), hence the favoring of primary alcohol formation.

That the behavior of the silyl-substituted epoxide **5c** toward i-Bu_2AlH and i-Bu_3Al is the reverse of that shown by alkyl and aryl-substituted epoxides **5a** and **5b** is not surprising. Electronic effects operative in the ring-opening reactions of α,β-epoxyalkylsilanes can rationally account for this behavior. Nucleophilic attack of $LiAlH_4$ or $LiAlD_4$ on **5c** is known to favor attachment of the hydride ion to the carbon α to silicon and the exclusive formation of the primary alcohol (eq 4):[18]



(4)

This regiochemistry is proposed to result via a transition state stabilized by partial pentacoordination of the hydride ion with silicon.[16] In the present study we could accordingly propose that the analogous reduction of **5c** with i-Bu_2AlH would be determined by a transition state like **11**.



Conversely, the tendency of i-Bu_3Al in THF to favor for-

(17) Eisch, J. J.; Rhee, S. G. *J. Organomet. Chem.* **1972**, *42*, C73.
(18) Eisch, J. J.; Traiinor, J. T. *J. Org. Chem.* **1963**, *28*, 2870.

mation of the secondary alcohol **6c** would be consistent with a transition state, as in **10**, again resembling a structure leading to the more stable carbenium ion **12a**. In this situation, however, the more stable carbenium ion site is the primary carbon, because the positive charge can be stabilized by carbon-silicon σ-bond hyperconjugation (**12b**).[19]

Experimental Section

General Procedures. All steps in the preparation, transfer, and main reactions of the organometallic reagents studied here were conducted under an atmosphere of anhydrous and oxygen-free argon. All solvents and apparatus were likewise freed of traces of dissolved or adsorbed moisture and oxygen and then maintained under argon. Methods and techniques for working under anhydrous and anaerobic conditions and for conducting standard chromatographic and spectrometric analyses have been described previously.[20]

Starting Materials and Products. Diisobutylaluminum hydride and triisobutylaluminum were obtained as neat reagents from Texas Alkyls Inc., Deer Park, TX. Diisobutylaluminum *sec*-butoxide was generated in situ by the **cautious** treatment of i-Bu_2AlH in heptane with 1 equiv of *sec*-butyl alcohol.

1,2-Epoxydecane and styrene oxide were commercially available and (epoxyethyl)triphenylsilane was prepared from the epoxidation of triphenylvinylsilane with *m*-chloroperbenzoic acid.[21]

The reaction products 1-decanol, 2-decanol, 1-phenyl-1-ethanol, and 2-phenyl-1-ethanol were purchased, while the 1-(triphenylsilyl)-1-ethanol and 2-(triphenylsilyl)-1-ethanol were synthesized by known procedures.[22]

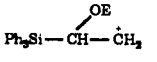
General Reduction Procedure. On a 1.0–10.0-mmol scale, the epoxide was dissolved in 10–50 mL of the solvent and then added slowly to 1.1 equiv of the aluminum hydride source, which was contained in a like volume of solvent and, in certain cases, was previously complexed with an equivalent of a Lewis base (R_3N or R_2AlOR'). The reaction mixture was allowed to stir at the given temperature for the stated reaction period (Table I).

If necessary, the reaction mixture was cooled to 25 °C and then **slowly and cautiously** treated with water (**gas evolution!**). Thereupon, dilute, aqueous HCl was added to give two clear layers. The separated organic layer was dried over anhydrous $MgSO_4$ and then the volatiles were removed in vacuo. The residue was analyzed by gas chromatography and separated by flash column chromatography.

Reductive Dehalogenation of 2-Chloro-1-(triphenylsilyl)-1-ethanol (8). A solution of 203 mg (0.61 mmol) of **8**, which was prepared from **5c** and $MeAlCl_2$,[16] and 120 mg (0.59 mmol) of tri-*n*-butyltin hydride in 15 mL of anhydrous toluene was heated at reflux for 8 h. The solvent was removed in vacuo and the residue subjected to flash chromatography on silica gel with 5% ethyl acetate in hexane. The isolated 1-(triphenylsilyl)-1-ethanol (**7c**) was obtained pure in 81% yield and was identified by comparison of its mp and its IR, ^1H NMR, and ^{13}C NMR spectral properties with those of an authentic sample.[18]

Acknowledgment. The research was supported by Texas Alkyls Inc. of Deer Park, TX, whose fostering of research on synthetic applications for organoaluminum reagents has been most appreciated.

(19) Any electrophilic attack on **5c**, such as where E = $MeAlCl_2$, is known to favor formation of the carbenium ion β to silicon



due to stabilization arising from carbon–silicon σ-bond hyperconjugation: Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829.

(20) Eisch, J. J. *Organometallic Synthesis*; Academic Press: New York, 1981; Vol. 2, p 194.

(21) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1976**, *41*, 2615.

(22) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 2870.

The Gas-Phase Basicity of Hydroxamic Acid Derivatives

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Introduction

One can understand at first sight, already from the name "hydroxamic acids" that the basic properties of these compounds (**1**) have been less investigated.[1] The crystallized hydrochloride of benzohydroxamic acid (**2**) was prepared,[2] and pK values in sulfuric acid have been reported for several substituted protonated benzohydroxamic acids.[3] As far as the site of protonation is concerned, several kinetic studies[3-5] have assumed that it is the carbonyl oxygen (see Scheme I, formula **1a** or **1b** with possible hydrogen bonds) rather than the nitrogen atom (**1c**), but without any proof, simply from an analogy with amides. The actual structure of the cation was seldom examined in contrast to the rather extensive discussion of the structure of the anion[1,6-8] and of the neutral molecule.[1,9,10] To our knowledge only the salt **2** was investigated by IR in dioxan[11] and by XPS in crystal,[12] in either case in favor of the structures **1a,b**. In a recent theoretical study[8] of formohydroxamic acid the structure **3a** was found slightly more stable than **3b** but distinctly more than **3c**. *N*-Alkyl-substituted hydroxamic acids seem to be more basic, and two forms of the cation (**1b** and **1c**; **1a** not considered) were claimed.[13] In aminohydroxamic acids the amino group is protonated first.[14]

In this paper we report the gas-phase basicities of acetohydroxamic acid (**4**) and of its *N*-methyl (**5**) and *O*-methyl (**6**) derivatives (Table I). In addition to the general interest—placing these compounds into the basicity scale[15]—we also hoped to get some information concerning the structure of the cation, particularly from a comparison with isosteric amides **7–9**.

Results and Discussion

The gas-phase basicities are collected in the table. The first conclusion emerges that hydroxamic "acids" are also relatively strong bases. In the whole scale[15] of the gas-phase acidity of organic acids (range of ~100 kcal), hydroxamic acids are placed relatively near the strongest acids, viz. at 27% of the whole range. But even in the scale of organic bases[15] (~110 kcal) they fall in the vicinity of strong bases (at 35% of the whole range). Compared with amides hydroxamic acids are stronger acids (by 15 kcal) and weaker bases (by 7 kcal). In all cases the reason is evidently the electron-attracting inductive effect of the oxygen atom.[16] In the case of the acidity of hydroxamic acids this effect is corroborated by a change of the mesomeric structure of the anion: the substitution by an oxygen induces an electron attraction from N and renders the mesomerism within the O=C—N unit better balanced. The two effects seem to strengthen each other in an efficient way.[17] In water solution[1] the difference in acidity between hydroxamic acids and amides is leveled. In the case of basicity even the order is reversed. A comparison with carboxylic acids is less easy to interpret: hydroxamic

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