the solvent gave a solid which was sublimed to afford 107 mg of (-)-**5** (70% yield): mp 140-141 °C (in a sealed tube); $[\alpha]^{17}_D$ -362° (*c* 0.448, $CHCl_3$); IR(KBr) 2935, 2880, 2850, 1470, 1460, 1312, 1280, 945, 938, 920, 895, 835, 805, 750 cm^{-1}; mass spectrum, *m/e* 148 (M^+), 119.

Anal. Calcd for $C_{11}C_{16}$: C, 89.12; H, 10.88. Found: C, 88.96; H, 10.99.

From (-)-30. Wolff-Kishner reduction of (-)-**30**, $[\alpha]^{20}_D$ -268° (122 mg, 0.753 mmol), with 100% hydrazine hydrate (0.12 mL) and KOH (60 mg) in triethylene glycol (1.5 mL) was carried out as described for the preparation of (±)-**6**. A solid obtained from the pentane eluates was sublimed at 50 °C (30 mm) to furnish 45 mg of (-)-**5** (40% yield): mp 138-140 °C (in a sealed tube); $[\alpha]^{18}_D$ -361° (*c* 0.510, $CHCl_3$).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.02; H, 10.65.

(-)-*C*$_2$-3,10-Dehydroditwistane (9). To an ice-cooled solution of (-)-**29**, $[\alpha]^{20}_D$ -31.2° (747 mg, 4.66 mmol), in ether (20 mL) was added an ethereal solution (53 mL) of diazomethane (ca. 1.1 g, 26 mmol) with stirring, and the stirring was continued for 12 h at 0 °C. The procedure described for the ring expansion of (+)-**26** gave a crude oily product which was treated with 100% hydrazine hydrate (0.8 mL) and KOH (450 mg) in triethylene glycol (10 mL). Wolff-Kishner reduction was carried out by following the same procedure described for the preparation of (±)-**6**, and the product was chromatographed on neutral alumina. Combined pentane eluates afforded a solid which was sublimed at 40 °C (5 mm) to give 545 mg of (-)-**9** (73% yield based on **29**): mp 42-43 °C (in a sealed tube); $[\alpha]^{20}_D$ -174° (*c* 0.803, $CHCl_3$); IR (KBr) 2920, 2850, 1455, 1438, 1330, 1285, 1270, 1230, 1158, 982, 940, 925, 870, 832, 780, 770, 748 cm^{-1}; mass spectrum, *m/e* 160 (M^+), 131.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.00; H, 10.02.

(-)-*C*$_2$-Ditwistane (6). Catalytic hydrogenation of (-)-**9**, $[\alpha]^{20}_D$ -174° (200 mg, 1.25 mmol), with 5% palladium on carbon (127 mg) in acetic acid (14 mL) was carried out as described for the preparation of (-)-**5**. The product was sublimed at 40 °C (5 mm) to give 157 mg of (-)-**6** (77% yield): mp 105-106 °C (in a sealed tube); $[\alpha]^{20}_D$ -538° (*c* 0.268, $CHCl_3$); IR (KBr) 2920, 2850, 1465, 1455, 1338, 1282, 1158, 1122, 1040, 918, 878, 845, 805, 740 cm^{-1}; mass spectrum, *m/e* 162 (M^+), 133.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.73; H, 11.26.

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Registry No. (-)-**5**, 74867-97-3; (-)-**6**, 74867-98-4; (±)-**6**, 74843-75-7; (-)-**8**, 74867-99-5; (-)-**9**, 74868-00-1; **17**, 592-57-4; **18**, 930-68-7; **19**, 64989-29-3; **19** semicarbazone, 65480-54-8; **20**, 74843-76-8; **22**, 74843-77-9; (±)-**24**, 74868-59-0; (+)-**26**, 62928-73-8; (-)-**28**, 74843-78-0; (-)-**29**, 74868-01-2; (-)-**30**, 74843-79-1.

Reactions of α,β-Epoxysilanes with Grignard Reagents. Generation and Trapping of α-Trimethylsilyl Aldehydes and Ketones

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α,β-Epoxysilanes react with Grignard reagents via initial rearrangement to generate α-silyl carbonyl compounds, which are trapped by the Grignard reagent to give β-hydroxysilanes. The reactions of epoxides **8** and **11** take place with very high stereoselectivity to form predominantly erythro β-hydroxysilanes **9** and **12**, respectively, which undergo stereospecific β-elimination reactions to give either cis or trans olefins in 96-98% isomeric purity.

Several years ago we initiated a study of the reactions of α,β-epoxysilanes with organometallic reagents as a possible route to diastereomerically pure β-hydroxysilanes, since we had previously shown that the olefin-forming β-elimination reactions of β-hydroxysilanes were stereospecific.[2] We found that a variety of α,β-epoxysilanes react with organocuprate reagents in a regio- and stereospecific manner at the carbon α to silicon to form diastereomerically pure β-hydroxysilanes.[3] (Stereospecific β-elimination reactions of these β-hydroxysilanes proved that the acid-catalyzed elimination reactions take place in an anti manner and that the base-induced elimination reactions take place in a syn manner.[3]) We also found that (trimethylsilyl)ethylene oxide (1) reacted with organolithium reagents[4] (PrLi, BuLi, *t*-BuLi) to give 2-(trimethylsilyl)-1-alkenes in moderate yield,[6] presumably via initial proton abstraction at the epoxide carbon α to silicon.[7]

The reactions of α,β-epoxysilanes with Grignard reagents[8] were found to give β-hydroxysilanes resulting from

(1) (a) Rutgers University. (b) Howard University (current address).
(2) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1133-1136 (1974); *J. Am. Chem. Soc.*, **97**, 1464-1468 (1975).
(3) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263-2264 (1975).
(4) Two previous examples of the reactions of α,β-epoxysilanes with organolithium reagents had been reported. The reaction of (triphenylsilyl)ethylene oxide with phenyllithium was reported to give tetraphenylsilane.[5] The reaction of (trimethylsilyl)ethylene oxide (1) with butyllithium (and other organometallic reagents) was investigated as a possible route to polymers [T. Tsuruta, S. Inoue, and H. Koenuma, *Makromol. Chem.*, **112**, 58-65 (1968)].
(5) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 2870-2876 (1963).
(6) P. F. Hudrlik, D. Peterson, and R. N. Misra, unpublished work. (See also footnote 9 in ref 3.) In the reaction of epoxide 1 with PrLi, $PrSiMe_3$ was identified as a byproduct.
(7) Eisch and Galle have shown that α,β-epoxysilanes and other substituted epoxides can be deprotonated by organolithium reagents, and the resulting intermediates can be used for the synthesis of more highly substituted epoxides: J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, **98**, 4646-4648 (1976); *J. Organomet. Chem.*, **121**, C10-C14 (1976).

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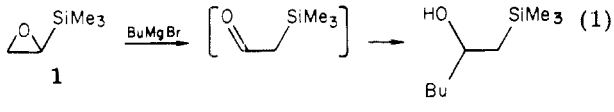
an initial Lewis acid catalyzed rearrangement of the epoxides to α-silyl aldehydes and ketones, followed by in situ trapping by the Grignard reagent.[9] Here we report the details of these reactions. The results are especially interesting since no general methods to prepare α-silyl aldehydes have been reported,[10] and our attempts to prepare and isolate simple α-trimethylsilyl aldehydes have been unsuccessful, suggesting these compounds are highly reactive, losing silicon with great facility or undergoing isomerization to silyl enol ethers. (In contrast, α-trimethylsilyl ketones can be prepared by several methods.[16])

Results and Discussion

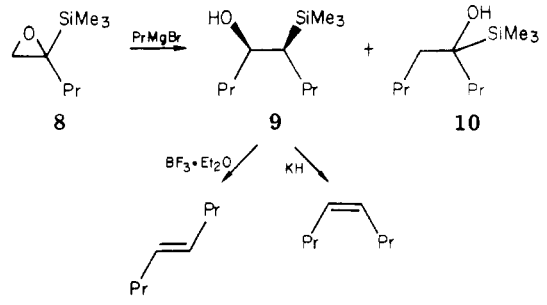
Treatment of (trimethylsilyl)ethylene oxide (1) with *n*-butylmagnesium bromide gave 1-(trimethylsilyl)-2-hexanol (2) in 85% yield (eq 1).[9a] The structure of the product was proven by independent synthesis from valeraldehyde and [(trimethylsilyl)methyl]magnesium chloride and by its β-elimination reaction using KH to form 1-hexene.



1 2 (1)

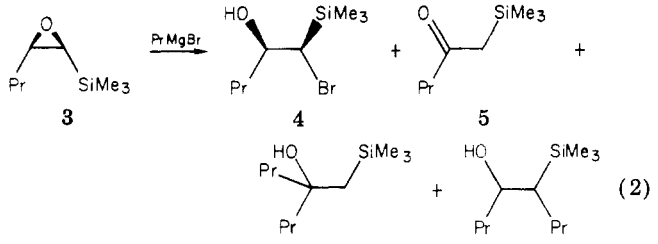
The reaction appears to involve an initial rearrangement of 1 to (trimethylsilyl)acetaldehyde, followed by trapping by the Grignard reagent. (Trimethylsilyl)acetaldehyde is an elusive compound which is difficult to isolate;[10,11] this reaction appears to be a means to generate and trap it in situ. The reaction is also interesting in that rearrangement of 1 to (trimethylsilyl)acetaldehyde in principle may have taken place by either of two pathways: epoxide opening at the carbon α to silicon with hydride migration or epoxide opening β to silicon with Me_3Si migration.

Scheme I



8 9 10

To gain information on the direction of epoxide ring opening, we studied the reaction of a Grignard reagent with the substituted epoxysilane 3.[9b] Treatment of epoxysilane 3 with *n*-propylmagnesium bromide initially produced a bromohydrin as the sole product (eq 2). This compound



3 4 5 6 7 (2)

was shown to be the α-bromo-β-hydroxysilane 4 by comparison of its NMR spectrum with that of the derived acetate (the hydrogen on the hydroxylic carbon was shifted downfield from δ 3.56 to 4.96 on acetylation) and by its acid-catalyzed β-elimination reaction which formed *trans*-1-bromo-1-pentene.[20] As the Grignard reaction progressed, 4 began to disappear, and three new products began to appear. The major product was shown to be the tertiary alcohol 6 by comparison with a sample prepared independently by treatment of 4-heptanone with [(trimethylsilyl)methyl]magnesium chloride. A minor product was shown to be 1-(trimethylsilyl)-2-pentanone (5).[12] These products are consistent with the α-opening pathway, with initial epoxide opening by $MgBr_2$ to give bromohydrin 4 (as the magnesium salt), followed by rearrangement of 4 to silyl ketone 5 and trapping by the Grignard reagent to form 6. The other minor product was shown to be 5-(trimethylsilyl)-4-octanol (7).[3]

The above results prompted us to study the rearrangements of a variety of α,β-epoxysilanes with $MgBr_2$, which we have reported elsewhere.[12] In every case, products resulting from α opening were observed. (These were the first reported examples which demonstrated α opening of α,β-epoxysilanes under acidic or electrophilic conditions.) In several cases (e.g., α,β-epoxysilane 3) we were able to isolate either an α-bromo-β-hydroxysilane (e.g., 4) or an α-silyl carbonyl compound (e.g., 5), depending on reaction conditions. However, we were unable to isolate simple α-silyl aldehydes from these reactions. The reaction of

(8) The reactions of (triphenylsilyl)ethylene oxide and (tribenzylsilyl)ethylene oxide with Grignard reagents have been reported (with no supporting spectral data) to give α-hydroxysilanes, products of ring opening β to silicon: A. Wende and A. Gesierich, *Plaste Kautsch.*, 8, 301–303 (1961); *Chem. Abstr.*, 56, 5993*f* (1962).

(9) A preliminary result was metioned in ref 3, footnote 9, and portions of this work were presented at the following meetings: (a) P. F. Hudrlik and D. Peterson, 168th National Meeting of the American Chemical Society, Atlantic City, NJ, Sept 1974; Abstracts, ORGN 99; (b) P. F. Hudrlik and A. M. Hudrlik, 169th National Meeting of the American Chemical Society, Philadelphia, PA, Apr, 1975; Abstracts, ORGN 14; (c) P. F. Hudrlik and R. N. Misra, 173rd National Meeting of the American Chemical Society, New Orleans, LA, March 1977; Abstracts, ORGN 93.

(10) (Triphenylsilyl)acetaldehyde has been prepared by the $MgBr_2$-induced rearrangement of (triphenylsilyl)ethylene oxide.[5,11] An attempt to prepare (phenyldimethylsilyl)acetaldehyde in a similar manner was unsuccessful,[11] and a number of attempts to oxidize (trimethylsilyl)-ethanol to (trimethylsilyl)acetaldehyde were unsuccessful.[11] We have prepared bis(trimethylsilyl)acetaldehyde[12] and tris(trimethylsilyl)acetaldehyde[13] by $MgBr_2$-induced rearrangements of the corresponding α,β-epoxysilanes. We have been unable to prepare (trimethylsilyl)acetaldehyde or simple α-trimethylsilyl (*n*-alkyl) aldehydes by rearrangements of α,β-epoxysilanes or by oxidations of β-hydroxysilanes, although we have prepared simple α-trimethylsilyl ketones by both of these methods.[2,12] (Trimethylsilyl)acetaldehyde has been recently reported (as a component of a mixture) from the reaction of (trimethylsilyl)ethylene oxide with a bromotrialkylstannane;[14] we have been unable to isolate pure (trimethylsilyl)acetaldehyde by this method. α-Trimethylsilyl aldehydes have been generated and trapped in the reactions of (α-chloroacyl)silanes with Grignard reagents.[15]

(11) J. W. Wilt, O. Kolewe, and J. F. Kraemer, *J. Am. Chem. Soc.*, 91, 2624–2631 (1969).

(12) P. F. Hudrlik, R. N. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona, and J. P. Arcoleo, *Tetrahedron Lett.*, 1453–1456 (1976).

(13) P. F. Hudrlik and G. P. Withers, unpublished work.

(14) G. S. Zaitsega, A. I. Chernyavskii, Y. I. Baukov, and I. F. Lutsenko, *J. Gen. Chem. USSR (Engl. Transl.)*, 46, 840–843 (1976).

(15) T. Sato, T. Abe, and I. Kuwajima, *Tetrahedron Lett.*, 259–262 (1978).

(16) Methods for preparing α-trimethylsilyl ketones include careful oxidations of β-hydroxysilanes,[2,17,18a,d] acylation reactions,[2,17,18a,d,19] reactions of (α-chloroacyl)silanes with Grignard reagents,[15] and rearrangements of α,β-epoxysilanes by $MgBr_2$,[12] MgI_2,[18b,d] or HI followed by BuLi.[18c,d] For a review, see Y. I. Baukov and I. F. Lutsenko, *Organomet. Chem. Rev., Sect. A*, 6, 355–445 (1970).

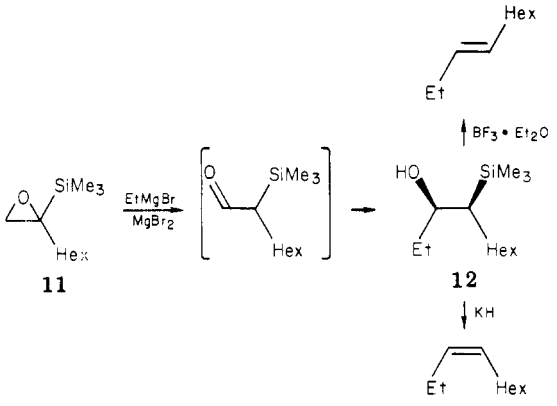
(17) R. A. Ruden and B. L. Gaffney, *Synth. Commun.*, 5, 15–19 (1975).

(18) (a) K. Utimoto, M. Obayashi, and H. Nozaki, *J. Org. Chem.*, 41, 2940–2941 (1976); (b) M. Obayashi, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, 1807–1810 (1977); (c) M. Obayashi, K. Utimoto, and H. Nozaki, *ibid.*, 1383–1386 (1978); (d) M. Obayashi, K. Utimoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 52, 2646–2652 (1979).

(19) (a) C. R. Hauser and C. R. Hance, *J. Am. Chem. Soc.*, 74, 5091–5096 (1952); (b) M. Demuth, *Helv. Chim. Acta*, 61, 3136–3138 (1978).

(20) P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withers, *J. Am. Chem. Soc.*, 99, 1993–1996 (1977).

Scheme II



(trimethylsilyl)ethylene oxide (1) with $MgBr_2$ gave the bromohydrin, 2-bromo-2-(trimethylsilyl)ethanol, but we were never able to isolate (trimethylsilyl)acetaldehyde from this reaction. [We have subsequently found that prolonged treatment of 1 with $MgBr_2$ results in mixtures of the bromohydrin and its trimethylsilyl ether. The latter compound may have resulted from reaction of the bromohydrin (MgBr salt) with (trimethylsilyl)acetaldehyde.] The reactions of the α-substituted α,β-epoxysilanes 8 and 11 with $MgBr_2$,[12,21] expected to yield α-(trimethylsilyl)-pentanal and α-(trimethylsilyl)octanal respectively, gave the corresponding silyl enol ethers.[22]

We have therefore studied the reactions of epoxysilane 8 with a Grignard reagent to see whether α-(trimethylsilyl)pentanal could be generated and trapped in situ. Treatment of 8 with *n*-propylmagnesium bromide yielded the desired β-hydroxysilane **9** as the major product together with the α-hydroxysilane **10**, an apparent product of β opening (Scheme I). To determine the stereoselectivity of the trapping of the silyl aldehyde, we carried out stereospecific acid- and base-induced β-elimination reactions on the β-hydroxysilane **9** (which was purified by preparative VPC). The resulting olefins, *cis*- and *trans*-4-octene, were obtained in high (96–98%) isomeric purity, with the acid-catalyzed reaction (BF_3·Et_2O) giving predominantly the trans isomer and the base-induced reaction (KH) giving the cis. This indicated that the trapping occurred in a highly stereoselective manner to form predominantly the erythro β-hydroxysilane.[9c]

Since the generation and trapping of α-silyl aldehydes is potentially useful, we have further studied the Grignard reaction in order to optimize conditions for β-hydroxysilane formation. For this purpose we used the higher molecular weight α,β-epoxysilane 11 since the ultimate olefin products would be less volatile. We found that treatment of epoxysilane 11 with ethylmagnesium bromide with additional magnesium bromide produced β-hydroxysilane **12** in 84% yield (Scheme II). A β-elimination reaction of **12** using BF_3·Et_2O produced *trans*-3-decene (90% yield) in 97% isomeric purity, and β-elimination using KH produced cis-3-decene (90% yield) in 98% isomeric purity.[9c] (Isomeric purities were determined by VPC analysis of the derived epoxides.)

These results indicate that simple α-silyl aldehydes can be generated and trapped efficiently by the Grignard reactions of α,β-epoxysilanes and that this trapping occurs in a highly stereoselective manner in accord with Cram's rule[23] to form erythro β-hydroxysiulanes. Kuwajima has recently noted a similar selectivity in the trapping of α-trimethylsilyl aldehydes generated from reactions of (α-chloroacyl)silanes with Grignard reagents.[15] Highly stereoselective addition reactions to α-silyl carbonyl compounds were first reported in the low-temperature DIBAL reduction of α-trimethylsilyl ketones[2] and have also been reported in the low-temperature addition of organometallics to α-trimethylsilyl ketones.[18a]

The reactions of α,β-epoxysilanes with Grignard reagents provide an interesting way to generate α-silyl aldehydes and ketones and trap them in situ to form β-hydroxysilanes. The generation of α-trimethylsilyl aldehydes is particularly noteworthy, since there is not yet any satisfactory way for preparing and isolating such compounds. The high degree of Cram's rule stereoselectivity in their reactions with Grignard reagents is also noteworthy, especially since the reactions were conducted at room temperature. α-Silyl aldehydes are interesting compounds which are potentially useful in organic synthesis, and methods for their preparation and isolation are currently under investigation in our laboratories.

Experimental Section

General Methods. Reactions were carried out under a nitrogen atmosphere, and transfers of liquids were accomplished with nitrogen-flushed syringes. The verb "concentrated" refers to removal of solvent under reduced pressure (water aspirator) by using a rotary evaporator. The term "evaporative distillation" refers to a short-path (bulb-to-bulb) distillation in a Kugelrohr apparatus under oil-pump vacuum; the temperature following in parentheses refers to the oven temperature.

Infrared (IR) spectra were obtained by using a Perkin-Elmer Infracord Model 137 spectrometer. Proton nuclear magnetic resonance (NMR) spectra were obtained by using a Varian T-60 spectrometer. Chemical shifts were measured in parts per million (δ) relative to an internal standard; chemical shifts of compounds containing a Me_3Si group were measured relative to $CHCl_3$ (δ 7.27); all others were measured relative to Me_4Si (δ 0.00). Mass spectra were obtained by using a Hitachi Perkin-Elmer Model RMU-7E instrument. Vapor-phase chromatographic analyses[24] were performed on a Varian Aerograph Model 90-P instrument using helium as the carrier gas; in many cases the retention time of a hydrocarbon standard under the given conditions is included.

Materials. Ether (as reaction solvent) and tetrahydrofuran (THF) were distilled from sodium and benzophenone. Methylene chloride was distilled. Boron trifluoride etherate was distilled under reduced pressure. α,β-Epoxysilanes 1,[3] 3,[3] 8,[12] and 11[25] were prepared as previously described. Samples of *cis*- and *trans*-4-octene and *cis*- and *trans*-3-decene were obtained from Chemical Samples Co.

Reaction of (Trimethylsilyl)ethylene Oxide (1) with *n*-Butylmagnesium Bromide. To *n*-butylmagnesium bromide in ether [from 141 mg (5.80 mmol) of magnesium, 11 mL of ether, and 425 mg (3.10 mmol) of *n*-butyl bromide] was added 245 mg (2.11 mmol) of (trimethylsilyl)ethylene oxide (1). The resulting mixture was stirred at room temperature for 17 h. Aqueous NH_4Cl

(21) P. F. Hudrlik and R. N. Misra, unpublished work.

(22) When the reactions were carried out in NMR tubes and followed by NMR, an aldehyde hydrogen (crude doublet) was observed within a few minutes; olefinic hydrogens corresponding to a silyl enol ether subsequently appeared as the aldehyde hydrogen disappeared. Aqueous workup after short reaction times led to mixtures containing considerable amounts of starting epoxide; we have been unable to isolate the α-trimethylsilyl aldehydes.

(23) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828–5835 (1952). See also J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, NJ, 1971.

(24) The following columns were used for VPC analysis: (a) 10% SE-30 on Chromosorb W, 10 ft × 0.25 in., aluminum; (b) 20% QF-1 on Chromosorb W, 10 ft × 0.25 in., aluminum; (c) 5% SE-30 on Chromosorb W, 4 ft × 0.25 in., aluminum; (d) 10% SF-96 on Chromosorb W, 20 ft × 0.25 in., aluminum; (e) 25% Carbowax 20M on Chromsorb W, 20 ft × 0.25 in., aluminum; (f) 10% DC-550 on Chromosorb W, 10 ft × 0.25 in., aluminum; (g) 20% Carbowax 20M on Chromosorb W, 10 ft × 0.25 in., stainless steel.

(25) P. F. Hudrlik, R. H. Schwartz, and J. C. Hogan, *J. Org. Chem.*, 44, 155–157 (1979).

was added, and the layers were separated. The organic layer was washed with saturated $NaHCO_3$, dried ($MgSO_4$), concentrated, and evaporatively distilled (110 °C), giving 313 mg (85%) of 1-(trimethylsilyl)-2-hexanol (2): IR (film) 2.9, 3.4, 8.00, 11.6, 11.9 μm; NMR (CCl_4) δ 3.70 (m, 1 H), 0.75 (d, J = 6.5 Hz, $SiCH_2$) overlapping with 2.0–0.7 (br) (total integration 11 H), 0.00 (s, 9 H). The IR and NMR spectra and VPC retention time corresponded to those of a sample of 1-(trimethylsilyl)-2-hexanol prepared from [(trimethylsilyl)methyl]magnesium chloride and valeraldehyde (ether, 10 h at room temperature). The mass spectrum showed m/e (relative intensity) 189 (2, presumed impurity), 159 (1), 157 (1), 156 (2, $M^+ - H_2O$), 147 (2), 141 (3), 117 (62), 101 (4), 91 (6), 84 (3), 75 (100), 73 (96). VPC analysis[24a] (130 °C, retention time for $C_{11}H_{24}$ = 4.86 min) showed the major peak (91% of peak area) at 5.12 min.

Reaction of *cis*-1-(Trimethylsilyl)-1-pentene Oxide (3) with *n*-Propylmagnesium Bromide. To an ice-cooled mixture of n-propylmagnesium bromide in ether [from 0.17 g (7 mmol) of magnesium and 0.57 mL (6.3 mmol) and n-propyl bromide in 10 mL of ether] was added 529.4 mg (3.34 mmol) of epoxysilane 3 in 10 mL of ether. The resulting mixture was stirred at 0 °C for 1.4 h and then added to saturated $NaHCO_3$ overlaid with ether. The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were dried (Na_2SO_4/$MgSO_4$), concentrated, and evaporatively distilled (135 °C), giving 0.71 g (89%) of the α-bromo-β-hydroxysilane 4 as a low-melting, oily, white solid: IR ($CHCl_3$) 2.8, 3.4, 8.01, 11.85 μm; NMR (CCl_4) δ 3.56 (m) and 3.30 (d, J = 2.5 Hz) (total integration 2 H), 1.8–0.8 (8 H), 0.13 (s, 9 H). The IR and NMR spectra were equivalent to those of samples of 4 which have been prepared from treatment of 3 with $MgBr_2$[12] and with HBr[20] and by treatment of *cis*-1-(trimethylsilyl)-1-pentene with NBA.[12] The mass spectrum showed m/e (relative intensity) 225 (0.2), 223 (0.2, $M^+ - CH_3$), 209 (0.4), 207 (0.4), 197 (7), 195 (7), 150 (17), 148 (16), 139 (15), 137 (12), 91 (18), 75 (90), 73 (100), 69 (58). VPC analysis[24b] (125 °C, retention time for $C_{15}H_{32}$ = 6.05 min) showed the major peak at 4.95 min (>99% of peak area). The α-bromo-β-hydroxysilane 4 was converted (acetic anhydride–pyridine, 95 °C, 3.3 h) to the acetate: IR (film) 3.4, 5.75, 7.31, 8.0, 9.80, 11.9 μm; NMR (CCl_4) δ 4.96 (t, J = 6.5 Hz, of d, J = 3 Hz, 1 H), 3.27 (d, J = 3 Hz, 1 H), 1.97 (s, 3 H), 2.0–0.8 (7 H), 0.10 (s, 9 H); the IR and NMR spectra were equivalent to those of the acetate of the bromohydrin from the reaction of *cis*-1-(trimethylsilyl)-1-pentene with NBA;[12] mass spectrum, m/e (relative intensity) 239 (0.4), 237 (0.4), 222 (3), 220 (3, M^+ – AcOH), 201 (6), 150 (4), 148 (4), 139 (10), 137 (10), 133 (31), 117 (100), 75 (55), 73 (47), 69 (33), 43 (59). As a further structure proof, the α-bromo-β-hydroxysilane 4 (from the reaction of 3 with PrMgBr) was treated with BF_3·Et_2O to form *trans*-1-bromo-1-pentene,[20] the product of anti β elimination.

A similar reaction of epoxysilane 3 with n-propylmagnesium bromide in ether was carried out at reflux. Thus a mixture of n-propylmagnesium bromide in ether [from 0.12 g (4.9 mmol) of magnesium and 0.43 mL (4.7 mmol) of n-propyl bromide in 7 mL of ether] and 0.37 g (2.3 mmol) of epoxysilane 3 in 7 mL of ether was stirred at 0 °C for 1 h and at reflux for 26 h. Workup[26] and evaporative distillation (125 °C) as described above yielded 0.35 g of colorless liquid. VPC analysis[24b] (122 °C) showed peaks at 5.6, 6.5, and 8.0 min in the area ratio of 3.4:16:1, respectively. The three components were isolated by preparative VPC.[24b]

The first component was identified as 1-(trimethylsilyl)-2-pentanone (5) by the following data: IR (CCl_4) 3.4, 5.92, 8.00, 11.7 μm; NMR (CCl_4) δ 2.22 (m) overlapping with 2.15 (s) (total integration 4 H), 1.50 (m, 2 H), 0.85 (t, J = 7 Hz, 3 H), 0.05 (s, 9 H); the IR and NMR spectra and VPC retention time of this compound were equivalent to those of a sample of 5 prepared by treatment of epoxysilane 3 with $MgBr_2$;[12] mass spectrum, m/e (relative intensity) 158 (6, M^+), 143 (26), 130 (14), 115 (72), 75 (72), 73 (100), 43 (17).

The major (second) component was identified as 4-[(trimethylsilyl)methyl]-4-heptanol (6) by the following data: IR (CCl_4) 2.7, 3.4, 8.07 μm; NMR (CCl_4) δ 1.5–1.1 (8 H), 1.1–0.7 (9 H), 0.00 (s, 9 H); mass spectrum, m/e (relative intensity) 187 (1, $M^+ - CH_3$), 184 (12, $M^+ - H_2O$), 169 (4), 159 (9), 143 (8), 115 (4), 99 (10), 91 (10), 75 (17), 73 (100), 59 (6). The IR and NMR spectra and VPC retention time of this compound were identical with those of a sample of 6 prepared from [(trimethylsilyl)methyl]-magnesium chloride and 4-heptanone (ether, 1 h at 0 °C and 3 h at room temperature).

The third component was identified as 5-(trimethylsilyl)-4-octanol (7) by comparison of its IR and NMR spectra with those of a sample prepared from the reaction of epoxide 3 with Pr_2CuLi.[3]

Similar reactions of epoxysilane 3 with n-propylmagnesium bromide run in the presence of pentadecane as an internal standard (1 h at 0 °C followed by 20 h at room temperature) and followed by VPC analysis[24b] of aliquots indicated that 4 was formed initially, that the percentage of 4 decreased, and that 5–7 appeared (and increased) in the product mixture as the reaction progressed.

Reaction of 2-(Trimethylsilyl)-1-pentene Oxide (8) with *n*-Propylmagnesium Bromide. To an ice-cooled solution of 445 mg (2.81 mmol) of epoxysilane 8 in 10 mL of ether was added 2.2 mL (3.1 mmol) of n-propylmagnesium bromide (1.4 M in ether). The resulting mixture was stirred for 1 h with warming to room temperature and for an additional 20 h at room temperature. Saturated NH_4Cl (10 mL) was added, and the organic layer was separated and washed with saturated $NaHCO_3$. The combined aqueous layers were extracted with four 10-mL portions of ether. The combined organic layers were dried ($MgSO_4$), concentrated, and evaporatively distilled (100 °C), yielding 529 mg of clear liquid. VPC analysis[24c] (110 °C, retention time for $C_{12}H_{26}$ = 3.4 min) showed two peaks (99% of peak area) at 3.4 and 4.8 min in an area ratio of 1:6, respectively. The two components were isolated by preparative VPC[24d] (150 °C).

The first component was identified as 4-(trimethylsilyl)-4-octanol (10) by the following data: IR (film) 2.9, 3.4, 8.00, 11.6, 11.9 μm; NMR (CCl_4) δ 1.6–0.7 (16 H), 0.00 (s, 9 H); mass spectrum, m/e (relative intensity) 185 (1), 184 (6, $M^+ - H_2O$), 169 (2), 99 (7), 75 (6), 74 (9), 73 (100).

The second component was identified as *erythro*-5-(trimethylsilyl)-4-octanol (9) by comparison of its IR and NMR spectra with those of an authentic sample[3] and by its β-elimination reactions. In a β-elimination reaction of 9 using acidic conditions [82 mg (0.41 mmol) of 9, 48 mg (0.42 mmol) of n-octane (internal standard), 10 mL of CH_2Cl_2, 0.40 mL (450 mg, 3.2 mmol) of BF_3·Et_2O, 1 h at room temperature], VPC analysis of the product indicated *trans*-4-octene containing less than 2% of the cis isomer was formed in 94% yield.[27] In a β-elimination reaction using basic conditions [51 mg of a 24% slurry of KH in oil (washed with pentane), 2 mL of THF, 12 mg (0.10 mmol) of n-octane (internal standard), and 24 mg (0.12 mmol) of 9, 1 h at room temperature], VPC analysis of the product indicated *cis*-4-octene containing 4% of the trans isomer was formed in quantitative yield.[27]

Reaction of 2-(Trimethylsilyl)-1-octene Oxide (11) with Ethylmagnesium Bromide–Magnesium Bromide. Preparation of *cis*- and *trans*-3-Decene. To an ice-cooled mixture of magnesium bromide in ether [from 1710 mg (9.10 mmol) of 1,2-dibromoethane in 5 mL of ether and 233 mg (9.59 mmol) of magnesium in 20 mL of ether[28]] were added 6.0 mL (12 mmol)[29] of ethylmagnesium bromide (2.08 M in ether) and 814 mg (4.06 mmol) of 2-(trimethylsilyl)-1-octene oxide (11). The resulting mixture was stirred for 15 min with warming to room temperature and for an additional 2 h at room temperature. Saturated NH_4Cl (15 mL) was added, the organic layer was separated and washed with saturated $NaHCO_3$, and the combined aqueous layers were extracted twice with ether. The combined organic layers were dried ($MgSO_4$), concentrated, and chromatographed on 25 g of Florisil. Elution with 1–2% ether in pentane yielded 830 mg of colorless liquid which was evaporatively distilled (125 °C), giving 787 mg (84%) of *erythro*-4-(trimethylsilyl)-3-decanol (12) as a

(26) The NMR and IR spectra of the crude product were consistent with its being a mixture of the components later isolated by preparative VPC.

(27) Yields and isomer ratios were determined by VPC[24e] (70 °C) with n-octane as an internal standard (relative detector response calibrated).

(28) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, Englewood Cliffs, NJ, 1954, p 33. See also H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, 28, 348–355 (1963).

(29) When epoxide 11 was treated with 1.3 equiv of $MgBr_2$ and 1.2 equiv of EtMgBr, the major product was the trimethylsilyl enol ether of octanal.

colorless liquid: IR (film) 2.9, 3.4, 8.02, 11.7, 11.9 μm; NMR (CCl_4) δ 3.64 (m, 1 H), 1.7–0.7 (20 H), 0.00 (s, 9 H); mass spectrum, *m/e* (relative intensity) 212 (2, $M^+ - H_2O$), 201 (3), 145 (2), 140 (6), 138 (9), 97 (10), 84 (10), 83 (9), 75 (38), 73 (100). VPC analysis[24f] (165 °C, retention time for $C_{15}H_{32}$ = 7.7 min) showed the major peak (98% of peak area) at 7.7 min.

A β-elimination reaction under acidic conditions was carried out with a solution of 198 mg (0.86 mmol) of **12** in 10 mL of methylene chloride to which was added 0.50 mL (560 mg, 3.9 mmol) of BF_3·Et_2O. The resulting solution was stirred at room temperature for 1 h. Saturated $NaHCO_3$ (10 mL) was added, and the organic layer was separated. The aqueous layer was extracted with three portions of ether. The combined organic layers were dried ($MgSO_4$), concentrated, and evaporatively distilled (room temperature), yielding 108 mg (89.6%) of clear liquid having IR and NMR spectra and a VPC retention time identical with those of a commercial sample of *trans*-3-decene.

A β-elimination reaction under basic conditions was carried out with a suspension of pentane-washed potassium hydride (from 558 mg of a 24% slurry in oil, 3.3 mmol) in 10 mL of THF to which was added 246 mg (1.07 mmol) of **12**. The resulting mixture was stirred for 1 h at room temperature. Saturated NH_4Cl (5 mL) was added, and the resulting mixture was poured into water overlaid with pentane. The organic layer was separated, washed with two portions of water, dried ($MgSO_4$), concentrated, and evaporatively distilled (50 °C), yielding 135 mg (90%) of clear liquid having IR and NMR spectra and a VPC retention time identical with those of a commercial sample of *cis*-3-decene.

As *cis*- and *trans*-3-decene were not separable with our VPC conditions, the isomeric purity of the elimination products was determined by using the derived epoxides, which were prepared by treatment of the β-elimination products with *m*-chloroperbenzoic acid in methylene chloride in the presence of Na_2HPO_4. (The products had IR and NMR spectra identical with those of samples of *trans*- and *cis*-3-decene oxide[30] prepared by analogous epoxidations of commercial samples of *trans*- and *cis*-3-decene.) VPC analysis[24g] (110 °C) of the product derived from β elimination under acidic conditions showed two major peaks (99% of peak area) at 11.9 and 14.3 min in a ratio of 97:3, corresponding to *trans*-3-decene oxide and *cis*-3-decene oxide, respectively. VPC analysis[24g] (110 °C) of the product derived from β elimination under basic conditions showed two major peaks (>99% peak area) at 11.9 and 14.3 min in a ratio of 2:98, corresponding to *trans*-3-decene oxide and *cis*-3-decene oxide, respectively.

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Registry No. **1**, 16722-09-1; **2**, 56183-59-6; **3**, 60484-84-6; **4**, 74844-81-8; **4** acetate, 74844-82-9; **5**, 60484-89-1; **6**, 74844-83-0; **7**, 52917-13-2; **8**, 60484-84-6; **9**, 55095-11-9; **10**, 74844-84-1; **11**, 62427-10-5; **12**, 74844-85-2; *trans*-4-octene, 14850-23-8; *cis*-4-octene, 7642-15-1; *trans*-3-decene, 19150-21-1; *cis*-3-decene, 19398-86-8; *trans*-3-decene oxide, 54724-75-3; *cis*-3-decene oxide, 54724-74-2; *n*-butyl bromide, 109-65-9; *n*-propyl bromide, 106-94-5; ethyl bromide, 74-96-4.

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Photobenzidine Rearrangements. 6. Mechanism of the Photodecomposition of 1,4-Diaryl-1,4-dialkyl-2-tetrazenes[1,2]

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The photodecompositon of the tetrazene *p*-$XC_6H_4N(Me)N{=}N(Me)NC_6H_4Y$-*p* (**1e**, X = Y = Me) in dimethoxyethane (DME) gave 47.4% of *p*-$XC_6H_4(Me)NN(Me)C_6H_4Y$-*p* (**2e**, X = Y = Me) and 39.6% of *N*-methyl-*p*-toluidine. When irradiation was carried out in the presence of increasing initial concentrations of *n*-BuSH, the yield of **2e** fell and leveled off at 6%. Similar experiments in cyclohexane showed that the yield of **2e** fell from 45.1% and leveled off at 10%. The data indicate that **1e** decomposes by a radical pathway and that the **2e** is formed partly within and partly outside of a solvent cage. Similar studies with **1d** (X = Me, Y = CO_2Et) in DME gave three hydrazines: **2d** (X = Me, Y = CO_2Et) in 13% and 14.7% yield, **2e** in 7.3% and 8.0% yield, and **2f** (X = Y = CO_2Et) in 14.9% and 21.2% yield. The formation of three hydrazines again indicates the formation and intermolecular recombination of methylarylamino radicals. Irradiation of **1d** in DME solutions containing *n*-BuSH caused a fall in the yield of **2e** to zero and a leveling off in the yield of **2d** to 6%. The yield of **2f** also fell but could not be monitored at high concentrations of *n*-BuSH because of overlapping high-pressure LC peaks. The results with **1d** are also consistent with a cage-recombination process (for **2d**) and an intermolecular recombination of radicals (for **2d–f**). The methylarylamines *p*-XC_6H_4NHMe and *p*-YC_6H_4NHMe (X = Me; Y = CO_2Et) were also formed from **1d**. A sixth product was the bis(arylamino)methane *p*-$YC_6H_4NHCH_2NHC_6H_4Y$-*p* (**4f**, Y = CO_2Et) in 14–32% yield (three runs). The origin of **4f** is believed to be the disproportionation of radicals *p*-YC_6H_4NMe, giving *p*-YC_6H_4NHMe and *p*-$YC_6H_4N{=}CH_2$ (**7f**). Hydrolysis of **7f** (by small amounts of water in the solvent) to *p*-$YC_6H_4NH_2$ (**6f**) and HCHO followed by addition of **6f** to **7f** would give **4f**. HCHO was found as a volatile product after irradiation. The formation of **4f** is further evidence for the formation and intermolecular reaction of arylamino radicals in the photodecomposition of 1,4-dialkyl-1,4-diaryl-2-tetrazenes.

1,4-Diaryl-1,4-dialkyl-2-tetrazenes have a prominent absorption band in the region of 350 nm. When irradiated in this region in solution such a tetrazene decomposes readily, losing nitrogen and forming a 1,2-diaryl-1,2-dialkylhydrazine. Decomposition appears to involve a singlet excited state,[3] but the mechanism of this conversion of a tetrazene into a hydrazine is not known with certainty. Analogous thermal conversions have received quite a lot of attention and are thought with little doubt to involve the formation and recombination of alkylarylamino radicals.[4–6] There is also firm evidence that radicals are

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