tion of the bromine concentration in the wave-length range of 280–340 $m\mu$, where the slit opening remained practically constant and the bromine absorption was relatively low. The "difference" absorbance (corrected for bromine absorbance) was plotted against the increasing bromine concentration until it reached a constant value, ΔA_∞, due to the complex alone. The slope in the logarithmic plot of $\Delta A/\Delta A_\infty - \Delta A$ *vs.* the bromine concentration yields the combining ratios (Fig. 3). The logarithmic ratio extrapolated to the 1.0 M bromine concentration affords the apparent stability constant. The foregoing method is described by Kingery and Hume[23] (method A).

Another method employed for determining the apparent stability constants of the quinolines was that described by Benesi and Hildebrand.[24] A comprehensive and critical review of the various methods of calculating stability constants has appeared recently.[25] In the present approach the stability constants were determined from the plot of the following function of the total concentrations, $[T_Q]\cdot[T_{Br_2}]/\Delta A$ *vs.* $[T_{Br_2}]$, where T_Q is the total initial concentration of the quinoline, T_{Br_2} the total initial concentration of the bromine, and ΔA the "difference" absorbance (Fig. 4 and 5). The slope yields the reciprocal of $\Delta\epsilon$, the difference between the molar absorptivities of the resulting complex and the respective quinoline, and the intercept provides the reciprocal of the product, $\Delta\epsilon\cdot K_c$, where K_c is the stability constant (method B).

The apparent stability constants obtained by these methods are summarized in Table I.

By study of the interaction of bromine with carbon tetrachloride in perfluorohydrocarbon solvents, it was shown that any bromine–carbon tetrachloride complexes are much weaker than the quinoline complexes examined. Hence, corrections for this solvent interaction can be neglected.

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(23) W. D. Kingery and D. N. Hume, *J. Am. Chem. Soc.*, **71**, 2393 (1949).

(24) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(25) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

Organosilicon Compounds with Functional Groups Proximate to Silicon. II. Lithium Aluminum Hydride Reduction of Epoxyethylsilanes[1]

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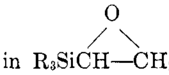
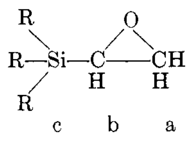
To evaluate the electronic impact of the silicon atom on the mode of behavior of an adjacent epoxide linkage, the lithium aluminum hydride reduction of a series of epoxyethylsilanes was investigated. Whether the R group in  $R_3Si\overset{O}{CH—CH_2}$ (I) was ethyl, benzyl, phenyl, or a *p*-substituted phenyl group, the predominant reduction product was the 2-substituted ethanol. That this primary alcohol arose from the direct hydride ion attack at the carbon alpha to silicon in I was demonstrated by a deuterium tracer study. The electronic factors involved in this novel reduction of epoxyethylsilanes are considered in the light of current theory.

In the previous paper of this series[1] the feasible synthesis of epoxyethylsilanes was reported for the first time. The chemical versatility of these systems offers an excellent opportunity for evaluating the electronic influence of the adjacent silicon atom on the behavior of the epoxide linkage (I). The present study reports results obtained from the lithium aluminum hydride reduction of epoxyethylsilanes (I), where both the electronic nature of R and the experimental conditions were varied. Presumably occurring by the nucleophilic attack of a complexed hydride ion,[3] this reaction offered the possibility of estimating the importance of three modes of attack. Not only could nucleophilic attack be expected at the secondary (Ib) and the primary carbons atoms (Ia) of the epoxide group, but also at the positive-polarized silicon atom (Ic). Indeed, as further research with epoxyethylsilanes has shown, certain nucleophiles, *e.g.*, phenyllithium and amines, effect carbon–silicon bond cleavage as the principal reaction.[4]



I

Results

In order to establish the general character of these epoxide reductions, the behavior of epoxyethyltriphenylsilane toward lithium aluminum hydride in tetrahydrofuran was examined in detail. Although the poor material balances obtained from reductions conducted at 66° indicated the occurrence of much carbon–silicon bond cleavage, reduction at 25° and usual work-up gave an excellent recovery of reduction products. When the epoxide–lithium aluminum hydride ratio was 1.0:3.25, the ratio of secondary to primary alcohols determined by gas chromatography was 1:6.5. Moreover, at an epoxide–lithium aluminum hydride ratio of 1.0:0.75, the primary alcohol was the sole product (Table I). Structures of the alcohols formed in reduction were verified by separating the isomers by column chromatography and comparing them with samples synthesized by unambiguous methods (Chart I). Thus, in contrast to other monosubstituted epoxides,[3] this epoxyethylsilane displays a decided preference for reduction to the primary alcohol, 2-(triphenylsilyl)-ethanol (III).

In assessing the significance of the foregoing, unexpected mode of epoxide reduction, it was desirable to show conclusively that the primary alcohol resulted from attack of the hydride ion at the secondary carbon atom. Since the lithium aluminum hydride reduction of epoxides with[3b] or without[5] Lewis acid additives can

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(1) Paper I in this series: J. J. Eisch and J. T. Trainor, *J. Org. Chem.* **28**, 487 (1963).

(2) (a) To whom inquiries should be addressed at the Department of Chemistry, Catholic University of America, Washington 17, D. C.; (b) Raybestos-Manhattan Predoctoral Fellow, 1959–1962.

(3) (a) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); (b) M. N. Rerick and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2356 (1962), and references cited therein.

(4) In unpublished studies of this laboratory phenyllithium has been shown to react readily with epoxyethyltriphenylsilane to yield tetraphenylsilane.

(5) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

CHART I

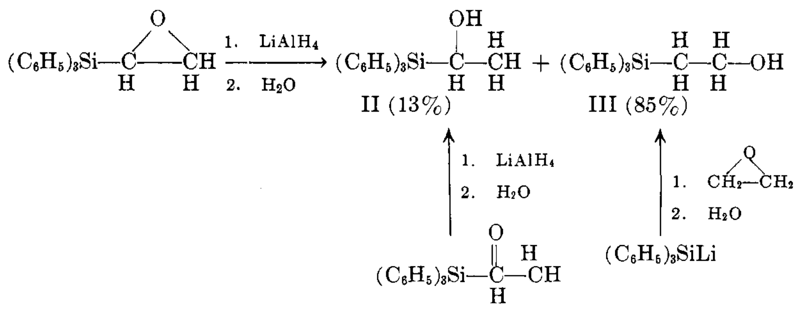
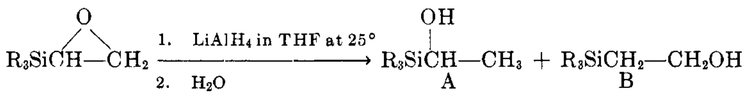


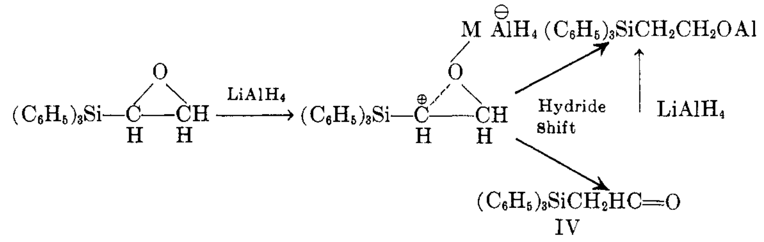
TABLE I

LITHIUM ALUMINUM HYDRIDE REDUCTION OF EPOXYETHYLSILANES



R group of epoxyethylsilane	Equiv. of hydride per mole of epoxide	Concn. of epoxide in THF, *M*	Material balance, %	Alcohol products, %		Other products, %
				A	B	
CH_3CH_2	13	0.02	72	0	98	$(CH_3CH_2)_3SiCH{=}CH_2$ (2)
$C_6H_5CH_2$	13	0.02	77	0	100	$C_6H_5CH_3$; $R_3'Si{-}H$[a]
C_6H_5	13	0.02	99	13	85	Unknown (2)
C_6H_5	15[b]	0.08	100	12	85[c]	Unknown (2)
C_6H_5	13[d]	0.40	99	13	86	...
C_6H_5	13[d,e]	0.40	53	...	...	...
C_6H_5	3	0.01	98	0	100	0
p-$CH_3O{-}C_6H_4$	13	0.02	100	<6	>94[f]	...
p-$CH_3{-}C_6H_4$	13	0.02	100	6	93	$R_3'Si{-}H$(1)[a]
p-$F{-}C_6H_4$	13	0.02	98	0	100	0
p-$CF_3{-}C_6H_4$	13	0.02	88	0	>90	Unknown (<10)[g]

[a] The nature of the R group in this silicon hydride impurity is unknown. [b] In this run a slurry of lithium aluminum deuteride in tetrahydrofuran was employed. [c] By n.m.r. spectroscopy this product was shown to be 2-(triphenylsilyl)ethanol-d_2. [d] These runs were conducted with a slurry of the hydride in tetrahydrofuran. [e] This run was conducted at the reflux temperature of tetrahydrofuran for 24 hr. [f] Yield is corrected for purity of initial epoxide. [g] The actual amount of unknown impurity is believed to be much less than 10%.



(1)

(2)

involve carbonium ion rearrangements, the principal mode of reduction of epoxyethyltriphenylsilane might occur directly (equation 1) or *via* rearrangement to the aldehyde (equation 2).

If the epoxide reduction were carried out with lithium aluminum deuteride, the deuterium should be found on the carbon atom alpha to silicon for a reaction involving direct hydride attack on the epoxide linkage (equation 1). On the other hand, if triphenylsilylethanal (IV) were an intermediate in the formation of the primary alcohol, the deuterium should be attached to the carbon atom beta to silicon. This problem is particularly well suited to solution by proton magnetic resonance spectroscopy, since the methylene groups of 2-(triphenylsilyl)ethanol (III) give two cleanly resolved triplet resonances signals at 1.68 and 3.70 δ, respectively. To verify the reasonable assumption that the signal of the methylene group alpha to silicon in III appears at 1.68 δ,[6] a sample of III specifically deuterated on the carbon beta to silicon was prepared. To this end, the previously unknown triphenylsilylethanal (IV)[7] was prepared by the magnesium bromide-catalyzed rearrangement of the epoxide and then was reduced with lithium aluminum deuteride. As anticipated, the n.m.r. spectrum of this 2-(triphenylsilyl)ethanol-d_1 (V) displayed a doublet resonance signal at 1.70 δ ($>\mathrm{C}\!<^{\mathrm{H}}_{\mathrm{H}}$) and a triplet at 3.70 δ ($>\mathrm{C}\!<^{\mathrm{H}}_{\mathrm{D}}$). This confirms the assignment of the high-field doublet to the methylene group alpha to silicon being split by the single proton on the -CHD- group (Chart II).

Subsequent reduction of epoxyethyltriphenylsilane with lithium aluminum deuteride and the separation of the resulting alcohols by column chromatography provided the deuterated 2-(triphenylsilyl)ethanol. Examination of this product by n.m.r. spectroscopy revealed a triplet resonance signal at 1.68 δ (Si-CHD-

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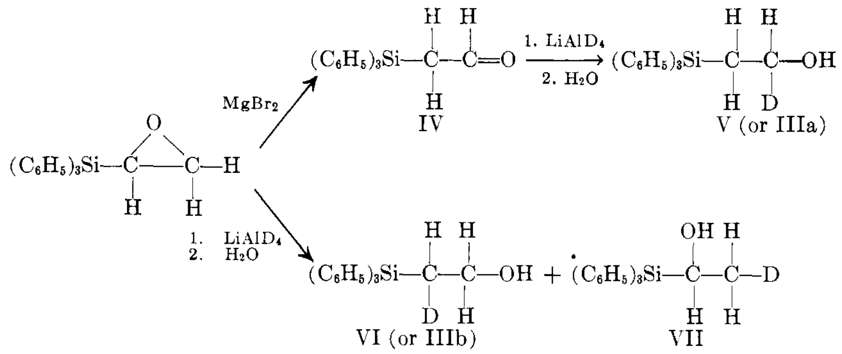
(6) The high-field n.m.r. resonance signals (low δ) of methyl and methylene groups adjacent to silicon is reflected in the use of tetramethylsilane as a high-field standard (δ = 0) in n.m.r. spectroscopy.

(7) The structure of this compound was verified by its infrared and n.m.r. spectra, as well as its lithium aluminum hydride reduction to 2-(triphenylsilyl)ethanol.

CHART II



split by -CH_2OH) and a doublet at 3.70 δ (-CH_2-OH split by (Si-CHD-). These data establish the structure of the principal epoxide reduction product as VI (Chart II). Therefore, it can be concluded that the primary alcohol is formed by direct hydride attack on the carbon alpha to silicon and that no preliminary rearrangement is involved.

To provide some insight into the role of the silicon atom in determining this unusual mode of epoxide reduction, a reduction product study was performed on a series of substituted epoxyethylsilanes bearing R groups of varying electronic character (I). The homogeneous reductions, carried out at 25.0 ± 0.1° in tetrahydrofuran, employed an epoxide–lithium aluminum hydride ratio of 1.0:3.25. Upon complete reduction the products obtained upon hydrolysis were analyzed by gas chromatography. In addition, quantitative column chromatography on Florisil was employed to substantiate the presence or absence of the isomeric ethanols and to isolate pure samples of the major and minor reduction products. The structures of the 1-substituted and 2-substituted ethanols were determined by a combination of methods: (a) elemental analysis; (b) infrared spectroscopy; (c) n.m.r. spectroscopy; and (d) comparison with authentic samples. The physical constants and analytical data for the new alcohols isolated in this manner are compiled in Table II.

TABLE II

ANALYTICAL DATA FOR NEW ALCOHOLS ISOLATED FROM THE LITHIUM ALUMINUM HYDRIDE REDUCTION OF EPOXYETHYLSILANES

		Analysis			
		Calcd.		Found	
Alcohol	M.p., °C.	% C	% H	% C	% H
(p-CH_3—C_6H_4)$_3$Si-CH_2CH_2OH	90–91	79.71	7.56	79.70	7.67
(p-CH_3—C_6H_4)$_3$Si-CH(OH)CH_3	88–88.5	79.71	7.56	79.85	7.76
(p-CH_3O—C_6H_4)$_3$Si-CH_2CH_2OH	81–82	70.01	6.64	69.76	6.83
(p-F—C_6H_4)$_3$Si-CH_2CH_2OH	83–84	67.01	4.78	66.91	5.04
(p-CF_3—C_6H_4)$_3$Si-CH_2CH_2OH	120–121	54.32	3.37	54.44	3.51
($C_6HC_5H_2$)$_3$Si-CH_2CH_2OH	40–41	79.71	7.56	79.69	7.48

The results of this comparative study are summarized in Table I. Several points deserve special comment. First, the predominant reduction product of these epoxyethylsilanes, regardless of the nature of the R group, is the 2-substituted ethanol B. Second, in runs where no 1-substituted ethanol A is reported, this negative result is based upon fruitless attempts to find such a minor component, involving gas and column chromatography, and infrared and n.m.r. spectroscopy. Both the crude reduction products and mother liquors from recrystallizations were examined in a search for this minor product. Third, the material balances after product work-up are, in general, excellent. Lower balances in the benzyl, ethyl, and p-trifluoromethylphenyl cases suggest some concurrent silicon–carbon bond cleavage. This assumption is further supported by the fourth point concerning Table I, namely, the appearance of silicon hydride by-products and the degradation of epoxyethyltriphenylsilane at higher temperatures. Fifth, the toluene detected as a by-product in the hydride reduction of epoxyethyltribenzylsilane does not seem to be an artifact arising from cleavage by the dilute sulfuric acid employed in the work-up. Although silicon–benzyl bonds may be cleaved slowly with concentrated sulfuric acid under certain circumstances,[8] such a cleavage is not a facile process.[9]

Discussion

Current views on the reduction of epoxides with lithium aluminum hydride hold that the reaction involves a bimolecular nucleophilic displacement on carbon proceeding by a S$_N$2-like mechanism.[3a] Monosubstituted ethylene oxides normally undergo reduction with hydride attack at the sterically more accessible carbon atom, leading to the secondary alcohol. More recently, evidence has come forward to indicate that Lewis acids (E = Li^+, AlX_3, AlH_3, etc.) may assist in such epoxide ring openings electrophilically.[3b,5] Indeed, the inclusion of aluminum halides can cause a complete reversal in the mode of ring opening, either by virtue of such electrophilic assistance favoring the more stable carbonium ion or because of carbonium ion rearrangements.[3b] In addition, with p-substituted styrene oxides and lithium borohydride the steric accessibility of the carbon atom attacked often is overrided by electronic factors, even in the absence of Lewis acid additives.[10]

In view of the findings of previous workers the most arresting observation in the present study is that the hydride reduction of epoxyethylsilanes (I) leads uni-

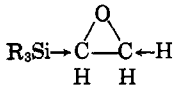
[8] H. H. Szmant, O. M. Devlin, and G. A. Brost, *J. Am. Chem. Soc.*, **73**, 3059 (1951).

[9] F. S. Kipping, *J. Chem. Soc.*, 223 (1907), reports that when ethylbenzyl-n-propylphenylsilane is heated with concentrated sulfuric acid at 80°, it is only the phenyl group which is readily cleaved.

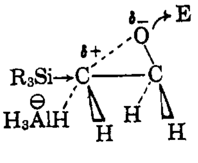
[10] R. Fuchs and C. A. Vander Werf, *J. Am. Chem. Soc.*, **76**, 1631 (1954).

formly to high yields of the primary alcohol, $R_3SiCH_2CH_2OH$. Deuterium tracer work in the case of epoxyethyltriphenylsilane demonstrated conclusively that hydride attack occurs directly at the secondary carbon atom. A fair assumption is that direct hydride attack is operative with the other epoxyethylsilanes also. Since lithium aluminum hydride reduction of epoxides is sensitive to steric effects,[3b] an understanding of the anomalous behavior of epoxyethylsilanes is desirable. As a careful examination of molecular models has shown, steric arguments would favor attack at the primary carbon atom. Therefore, another explanation must be sought.

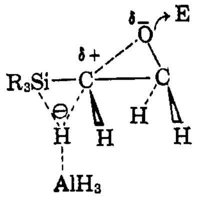
Three electronic effects may be operative in these epoxide reductions. First, consideration of ground state susceptibilities of the two carbon atoms to nucleophilic attack indicates that reaction should occur principally at the terminal carbon because of the inductive release of electrons by silicon along the σ-bond ($X_{Si} = 1.8$, $X_H = 2.1$; $X_C = 2.5$) (VIII). Second, if C–O bond breaking has proceeded to a significant extent in the transition state, then the incipient carbonium ion on the secondary carbon atom will be more stabilized than that on the primary carbon. Here the inductive electron release of the adjacent silicon atom would aid attack at the secondary carbon atom in the transition state (IX). Third, the pronounced tendency of numerous Si–Z bond cleavages to occur *via* nucleophilic attack on silicon strongly implicates the available d-orbitals of this element.[11] In the present situation preferential hydride attack on the secondary carbon suggests that the silicon's d-orbitals and the electron-deficient secondary carbon may cooperate in stabilizing a three-center transition state (X).[12]



VIII

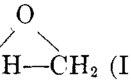


IX



X

That the primary alcohol is the predominant product in the reduction of epoxyethylsilanes rules out any significant dependence on the ground state nucleophilic susceptibilities of the carbon atoms (factor 1: VIII). Either of the other electronic viewpoints (IX and X) would be compatible with the experimental findings. However, other considerations tend to favor X.

First, within the series of epoxyethylsilanes, R_3Si-  $\overset{O}{\overbrace{CH—CH_2}}$ (I), the apparent yield of secondary alcohol decreased in the order, R = phenyl > *p*-tolyl ~ *p*-anisyl > *p*-fluorophenyl [~ *p*-trifluoromethylphenyl ~ benzyl ~ ethyl] (Table I). Although no secondary alcohols were detected with last three bracketed systems, the lower material balances force some degree of caution in these cases.[13] The fact that the amount of secondary alcohol bears no obvious relationship to the electron-donating or withdrawing properties of the R_3Si group,[14] tends to weaken the argument for the transition state depicted in IX. The tri-*p*-fluorophenylsilyl group would be expected to less electron-donating than the triphenylsilyl group, yet the former yields only primary alcohol. The three-center transition state given in X is more in accord with the observed behavior of these epoxysilanes. Here the electron-withdrawing character of R can promote partial nucleophilic interaction with silicon's d-orbitals by depleting the electron cloud about silicon. Conversely, electron-donating groups can facilitate C–O bond breakage by enhancing silicon's inherent electron release.

Secondly, the observed cleavage of silicon–carbon bonds during the reduction and the frequent detection of silicon hydrides upon work-up attest to the feasibility of hydride attack at silicon in these systems. Finally, the primary alcohol was the sole reduction product of epoxyethyltriphenylsilane when the excess of hydride was sharply reduced. Under these conditions at least some of the reduction must be performed by $LiAl[(OR)_nH_{4-n}]$. Such hydrides appear to be milder, more selective reducing agents.[15] If a straightforward S_N2 attack (IX) is assumed, this absence of steric hindrance is unexpected. Further work will consider this intriguing aspect.

Experimental[16]

Starting Materials.—The preparation and purification of the requisite epoxyethylsilanes were conducted according to previously published procedures.[1] The epoxides were recrystallized or redistilled just before use, and their purity was checked by a combination of melting point, infrared spectral and gas chromatographic criteria.

The lithium aluminum hydride and the lithium aluminum deuteride were obtained from Metal Hydrides Inc., Beverly, Mass., and were at least of 95 and 98% purity, respectively. A standard solution of lithium aluminum hydride in tetrahydrofuran[17] was prepared for epoxide reduction studies under homogeneous conditions. Thus a slurry of 25 g. of powdered lithium aluminum hydride in 1 l. of pure tetrahydrofuran (*vide infra*) was stirred at the reflux temperature for 24 hr. and at room temperature for 24 hr. Several filtrations through a sintered glass filter of medium porosity furnished a very slightly turbid solution. This solution was analyzed for hydride concentration in the fol-

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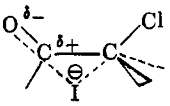
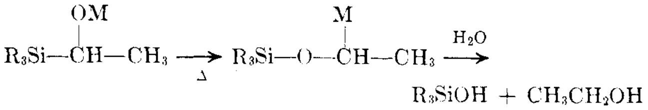
[11] C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp. 103–113.

[12] An analogous transition state has been suggested to explain the rapid displacement of chloride ion by iodide ion in α-chloro ketones.



Cf. P. D. Bartlett in H. Gilman, Ed., "Organic Chemistry–An Advanced Treatise," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 35.

[13] The point of concern here is that secondary alcohol by-products might be preferentially destroyed by the following well known rearrangement.



$$R_3Si—\overset{\overset{OM}{|}}{C}H—CH_3 \xrightarrow[\Delta]{} R_3Si—O—\overset{\overset{M}{|}}{C}H—CH_3 \xrightarrow{H_2O} R_3SiOH + CH_3CH_2OH$$

Cf. A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Am. Chem. Soc.*, **81**, 981 (1959). However, the failure to detect any silanol, R_3SiOH, or disiloxane, $R_3Si–O–SiR_3$, in the reduction products tends to dismiss such a rearrangement as the cause of the low material balances.

[14] In the previous paper of this series (ref. 1) a study of the CH_2 wag frequency of vinylsilanes showed significant differences in the electronic character of such groups as the tris(*p*-trifluoromethylphenyl)silyl *vs.* the triphenylsilyl groups, and the triethylsilyl *vs.* the trichlorosilyl groups.

[15] (a) H. C. Brown and R. F. Mc Farlin, *J. Am. Chem. Soc.*, **78**, 252 (1956); **80**, 5372 (1958); (b) H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958); (c) H. C. Brown and A. Tsukamoto, *ibid.*, **81**, 502 (1959).

[16] All melting points are uncorrected. Procedures involving the preparation and reaction of metal hydride solutions were conducted under an atmosphere of dry, oxygen-free nitrogen.

[17] T. Higuchi and D. A. Zuck, *J. Am. Chem. Soc.*, **73**, 2676 (1951).

lowing manner. A 5.00-ml. aliquot of the hydride solution was added to a titration flask containing 15 ml. of pure tetrahydrofuran and 5 drops of a 1% solution of N-phenyl-*p*-aminoazobenzene in dry benzene. The resulting red solution was titrated with a standard solution of *n*-butyl alcohol in benzene, the abrupt color change from red to yellow signaling the end point. (Both the titrant and the hydride solution sample were maintained under a dry nitrogen atmosphere during analysis.) On the basis of this titration the tetrahydrofuran solution was found to be 0.630 ± 0.003 *M* in lithium aluminum hydride. Such solutions could be stored under a nitrogen atmosphere for several weeks without appreciable loss in activity.

All chromatographic separations were carried out on adsorption columns built with Florisil (magnesium silicate, 60–100 mesh, Floridin Co., Tallahassee, Fla.) and reagent-grade petroleum ether (b.p. 30–60°). Only dry, reagent-grade solvents were used in column chromatography and in the hydride reactions proper. Tetrahydrofuran was purified in the customary fashion.[1]

The n.m.r. spectra of the samples dissolved in carbon tetrachloride solution were obtained with a Varian 60-Mc. nuclear magnetic resonance spectrometer. The gas chromatographic analyses were performed on a Barber-Colman gas chromatograph, Model 10, employing a strontium-90 ionization detector system.

Rearrangement of Epoxyethyltriphenylsilane. Preparation of (Triphenylsilyl)ethanal (IV).—To a stirred solution of 17.6 mmoles of magnesium bromide etherate in 50 ml. of purified *n*-butyl ether was added over 5 min. a solution of 1.00 g. (3 mmoles) of epoxyethyltriphenylsilane in 50 ml. of *n*-butyl ether. The magnesium bromide etherate was prepared by the addition of bromine to a suspension of magnesium metal in ethyl ether and was analyzed by the Volhard method.[18] The reaction mixture was then heated at 60° for 5 hr. (a precipitate formed after 20 min. at 60°), cooled and treated with 80 ml. of freshly purified *p*-dioxane. Thereafter the resulting slurry was stirred for 12 hr. at room temperature and then filtered. The collected salts were washed with benzene, and the combined organic extracts were freed of solvent. The extract residue, upon dissolution in ethyl ether and cooling, deposited 0.73 g. (73%) of (triphenylsilyl)ethanal, m.p. 110–116°. Recrystallization from ethyl ether gave an analytical sample, m.p. 115.5–116°.

Anal. Calcd. for $C_{20}H_{18}OSi$: C, 79.43; H, 5.99. Found: C, 79.68; H, 6.15.

The infrared spectrum of this compound displayed an intense absorption at 1700 cm.$^{-1}$. However, neither the infrared spectrum of the pure substance nor of the crude product showed any band at 1640 cm.$^{-1}$ (methyl triphenylsilyl ketone[19]). The n.m.r. spectrum of the aldehyde as a 15% solution in carbon tetrachloride with tetramethylsilane as an internal standard displayed the following resonance signals (in δ values): triplet centered at 9.62 ($\overset{\mathrm{H}}{\overset{|}{\mathrm{—C}}}\mathrm{=O}$), multiplet at 7.38 (phenyl protons), and doublet at 2.97 ($-CH_2-$). This spectrum is completely consonant with the assigned structure.

Treatment of the aldehyde with an ethanolic solution of *p*-nitrophenylhydrazine and recrystallization of the product from benzene provided the *p*-nitrophenylhydrazone, m.p. 228–229°.

Anal. Calcd. for $C_{26}H_{23}N_3O_2Si$: N, 9.60. Found: N, 9.39.

When the rearrangement of the epoxide was repeated with only a 30 min. stirring period after addition of *p*-dioxane and the total crude product was purified by column chromatography on Florisil, two products were isolated. Elution of the chromatogram with benzene furnished a 10% yield of triphenylsilanol (m.p. 150–153°), identified by mixture melting point and infrared spectroscopy. Subsequent elution of the column with chloroform allowed the isolation of the aldehyde.

Reduction of (Triphenylsilyl)ethanal. A. With Lithium Aluminum Hydride.—To a stirred suspension of 0.25 g. (6.6 mmoles) of lithium aluminum hydride in 30 ml. of tetrahydrofuran was added dropwise a solution of 0.30 g. (1.0 mmole) of (triphenylsilyl)ethanal in 20 ml. of tetrahydrofuran. The reaction mixture was stirred at the reflux temperature for 6 hr. and then treated with water. Collection of the precipitate furnished 0.32 g. of product, melting 74–90°. Recrystallizations from cyclohexane and chromatography of the mother liquors (elution with chloroform) gave 0.14 g. (47%) of colorless 2-(triphenylsilyl)ethanol (III), m.p. 96–97°. Comparison with an authentic sample of the β-alcohol (m.p. 96.5–98°; lit.[20] m.p. 99–100°) by infrared spectroscopy and mixture melting point verified its identity.

B. With Lithium Aluminum Deuteride.—To a stirred slurry of 0. 50 g. (12 mmoles) of lithium aluminum deuteride in 100 ml. of tetrahydrofuran was added dropwise a solution of 0.60 g. (2.0 mmoles) of (triphenylsilyl)ethanal in 50 ml. of tetrahydrofuran. The reaction mixture was stirred at room temperature for 8 hr., cooled, hydrolyzed, and then filtered. The separated organic phase was dried with anhydrous magnesium sulfate and the solvent thereafter evaporated. The residue weighed 0.60 g. and melted at 93–96°. Recrystallization from cyclohexane provided 0.51 g. (83%) of 2-(triphenylsilyl)ethanol-*d*₁ (IIIa), m.p. 99–100°. The n.m.r. spectrum displayed resonance signals (in δ values, relative to tetramethylsilane) at 1.70 (doublet, $>C<^{H}_{H}$) and 3.70 (triplet, $>C<^{H}_{D}$).

Reduction of Epoxyethyltriphenylsilane. A. With Lithium Aluminum Hydride.—To a slurry of 1.25 g. (0.033 mole) of lithium aluminum hydride in 200 ml. of tetrahydrofuran was added in one portion a solution of 3.02 g. (0.010 mole) of epoxyethyltriphenylsilane in 25 ml. of tetrahydrofuran. The reaction mixture was stirred at room temperature for 8 hr. and thereupon treated with water. The system was filtered and the collected solid triturated with portions of benzene and of chloroform. The combined organic extracts were dried with anhydrous calcium sulfate and the solvent was then evaporated. By gas chromatography the residue (3.00 g., 99%) was shown to be a 1:6.5 mixture of 1-(triphenylsilyl)ethanol (II)—2-(triphenylsilyl)ethanol (III) (*vide infra*). After two recrystallizations from cyclohexane 2.50 g. (83%) of 2-(triphenylsilyl)ethanol, m.p. 96–98°, were obtained. Comparison with an authentic sample by infrared spectroscopy and mixture melting point verified its identity. Moreover, a mixture with authentic 1-(triphenylsilyl)ethanol melted depressed and over a range.

When the foregoing reaction was conducted at the reflux temperature of tetrahydrofuran for 24 hr., an identical work-up procedure yielded only 1.60 g. (53%) of the crude alcohol mixture. This result implies that hydride cleavage of silicon–carbon bonds had occurred.

B. With Lithium Aluminum Deuteride.—Analogous to the foregoing procedure, a slurry of 1.39 g. (0.033 mole) of lithium aluminum deuteride in 60 ml. of tetrahydrofuran and 3.02 g. (0.010 mole) of the epoxide was stirred at room temperature for 8 hr. Usual work-up, drying of the organic extracts with anhydrous magnesium sulfate and solvent evaporation provided 3.01 g. of the crude alcohol mixture. By gas chromatography the ratio of the 1-substituted to 2-substituted alcohol was 1:7.1.

Thereafter the mixture of alcohols was separated by column chromatography on Florisil (*vide infra* for details concerning the isolation of the alcohols from the lithium aluminum hydride reduction of epoxyethyltriphenylsilane in an homogeneous medium). That the principal product thus isolated was 2-(triphenylsilyl)ethanol-*d*₂ (IIIb) (m.p. 98–99°) was established by examination of its n.m.r. spectrum. In δ values, relative to tetramethylsilane, a triplet appeared at 1.67 ($>C<^{H}_{D}$) and a doublet at 3.70 ($>C<^{H}_{H}$). Comparison with the n.m.r. spectrum of authentic 2-(triphenylsilyl)ethanol-*d*₁ confirmed the position of the deuterium.

Lithium Aluminum Hydride Reduction of Epoxyethylsilanes in Homogeneous Solution. A. General Procedure.—To a solution of 25.0 ± 0.5 mmole (by titration) of lithium aluminum hydride in 400 ml. of tetrahydrofuran was added with stirring a solution of 8.00 ± 0.05 mmole of the epoxyethylsilane in 50 ml. of tetrahydrofuran. The solution was stirred for 8–25 hr. in a constant temperature bath at 25.0 ± 0.1°. Then 250 ml. of anhydrous ethyl ether was added to decrease the solubility of water in the organic layer. The cooled reaction mixture was hydrolyzed either by the careful dropwise addition of 120 ml. of 0.3 *M* aqueous sulfuric acid (cooled to 10°) or of water. After separation of layers the aqueous layer was extracted with ethyl ether. The combined organic extracts were washed with sodium carbonate solution and then dried over anhydrous magnesium sulfate. The details of the isolation and further purification of reaction products are given subsequently for the individual

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[18] J. P. Horwitz, *J. Am. Chem. Soc.*, **79**, 62 (1957).

[19] A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).

[20] H. Gilman, D. Aoki, and D. Wittenberg, *ibid.*, **81**, 1107 (1959).

reductions. The physical constants and analytical data for the alcohols isolated from these hydride reductions are compiled in Table II.

The material balances reported in Table I are based upon the weight of the dried crude product isolated. Except in the reduction of epoxyethyltriethylsilane, the accuracy of these values is estimated to be ±1%. In the ethyl case the material balance had to be determined indirectly (*cf.* reduction of epoxyethyltriethylsilane), since the volatile liquid product was difficult to separate from the solvent quantitatively.

The product ratios given in Table I, determined by gas chromatography of the crude reaction products, are averages from several injections which agreed within ±1%. Based upon the analysis of a known mixture of epoxyethyltriphenylsilane and triphenylvinylsilane, the accuracy of these results is estimated to be ±2%. Moreover, product ratios from duplicate reductions of epoxyethyltriphenylsilane agreed within ±1%. Gas chromatography could not be used to determine product ratios in the *p*-anisyl (decomposition) and *p*-trifluoromethylphenyl (negative ionization characteristics) cases. Where only one peak was shown in the gas chromatogram, column chromatographic treatment and recrystallization were employed to test the homogeneity of the product.

B. **Epoxyethyltriethylsilane.**—The dried organic extract was concentrated to about 15 ml. by distillation of the organic solvent through a Vigreux column. The residue was transferred to a 25-ml. volumetric flask and diluted to the mark with tetrahydrofuran. A 10.0-ml. aliquot was concentrated and examined by infrared spectroscopy and gas chromatography. (A 6-ft., 20% silicone oil-on-firebrick column at 195°.) In this manner the product was shown to contain 98% of 2-(triethylsilyl)-ethanol and 2% of triethylvinylsilane (absent in starting epoxide). Comparison with the chromatographic retention times and spectra of authentic samples of 1-(triethylsilyl)ethanol and 2-(triethylsilyl)ethanol[21] confirmed the exclusive presence of the primary alcohol.

To the remaining 15.0 ml. of product solution was added 0.130 g. (0.92 mmole) of triethylvinylsilane. Gas chromatography of this solution gave integrated areas of 0.13 and 0.45 for the olefin and alcohol, respectively. After correction for the 2% of impurity and upon the assumption that the areas are proportional to mole fractions, these results (0.12:0.45) represent a material balance of at least 72%. The most probable source of error lies in the evaporation of the 10.0-ml. aliquot. If some of the minor product is lost, the figure of 0.12 would be too high and the actual material balance more attractive.

Finally, the infrared spectrum of the crude reaction product had no absorption bands indicative of $\equiv$Si—H, $\equiv$Si—O—H or $\equiv$Si—O—Si$\equiv$ linkages.

C. **Epoxyethyltribenzylsilane.**—The dried organic extract was concentrated and finally evaporated to dry constant weight by warming under reduced pressure. The residual oil (77% material balance) was shown by infrared spectroscopy and gas chromatography (3 ft., 5% silicone gum rubber-on-firebrick column at 200°) to contain no epoxide and apparently only 2-(tribenzylsilyl)ethanol.[22] Chromatography of the crude product on Florisil and elution with ethyl ether–petroleum ether (b.p. 30–60°) (1:9) yielded a series of hydroxylic solids, m.p. 40–41°, after a slight forerun of material containing an –Si–H infrared absorption at 2150 cm.$^{-1}$. Quantitative column chromatography and infrared examination of the various eluted fractions gave no indication of the presence of the secondary alcohol. The criteria for the detection of any 1-substituted ethanol were its invariable elution from the Florisil column before the 2-substituted ethanol and its infrared band at 890 cm.$^{-1}$.

Recrystallization of the main product from *n*-hexane provided an analytical sample, m.p. 40–41°. The n.m.r. spectrum of this alcohol confirmed it to be 2-(tribenzylsilyl)ethanol: cleanly resolved high (Si–CH$_2$) and low (CH$_2$–OH) field triplets, together with intermediately situated benzylic and hydroxylic proton resonances, respectively.

The lower material balance in this reduction prompted an examination of the recovered reaction solvent. The ultraviolet spectrum of the reaction solvent residue in pure tetrahydrofuran verified the presence of toluene; $\lambda_{\max}^{\text{THF}}$ 268, 262, and 257 mμ.

D. **Epoxyethyltriphenylsilane.**—This reduction was conducted and worked up as in part B. After determination of the product ratio of secondary alcohol–primary alcohol (1:6.5) by gas chromatography on a 3-ft., 5% silicone gum rubber-on-firebrick column, the alcohols were then separated by column chromatography on Florisil. Elution with ethyl ether–petroleum ether (b.p. 30–60°) (1:9) provided the 1-(triphenylsilyl)ethanol first. This product upon recrystallization from cyclohexane melted at 100–101°. Infrared spectral and mixture melting point comparison with an authentic sample confirmed its identity.[23] The infrared absorption at 890 cm.$^{-1}$ is especially characteristic.

Further chromatographic elution gave the pure 2-(triphenylsilyl)ethanol. Recrystallization from cyclohexane provided a m.p. of 99–100°. Besides analogous spectral and melting point comparisons with an authentic sample, it was observed that a mixture with the secondary alcohol melted over the range, 75–80°. The infrared absorption at 925 cm.$^{-1}$ was characteristic.

In a run conducted as in the foregoing procedure, but employing 5.6 mmoles of lithium aluminum hydride and 6.9 mmoles of epoxyethyltriphenylsilane in 500 ml. of tetrahydrofuran, the sole product detected upon the usual work-up was 2-(triphenylsilyl)ethanol.

E. **Epoxyethyltri-*p*-anisylsilane.**—Since it was not possible to analyze the crude reaction product by gas chromatography (due to decomposition), an n.m.r. spectrum was obtained. The spectrum of the crude product was completely consistent with the structure of 2-(tri-*p*-anisylsilyl)ethanol, and there was no indication of the presence of the secondary alcohol. As expected, there was a high-field triplet due to the methylene group alpha to the silicon atom (on the basis of the deuterium study in the reduction of epoxyethyltriphenylsilane), a strong singlet due to the methoxyl protons and a peak on the high-field side of the latter resonance signal. By estimation from other 2-substituted ethanols the triplet due to the methylene group alpha to the hydroxyl group should lie downfield from tetramethylsilane at about the same position as the methoxyl protons. It is concluded, therefore, that this latter triplet is partially overshadowed by the methoxyl proton resonance.

As n.m.r. examination would not detect minor constituents, the crude product was chromatographed carefully on Florisil. Elution with 10% ethyl ether in cyclohexane and then with a 20% concentration gave 11% of product whose infrared spectrum showed it to be tri-*p*-anisilvinylsilane (probably present in starting epoxide). Elution with ethyl ether provided a fraction containing bands characteristic of the primary alcohol, together with a modest band at 875 cm.$^{-1}$. This may indicate a content of <6% of the secondary alcohol. Further elution with ethyl ether yielded 84% of 2-(tri-*p*-anisylsilyl)ethanol, which upon recrystallization from cyclohexane melted at 81–82°.

F. **Epoxyethyltri-*p*-tolylsilane.**—Gas chromatography of the crude product revealed a 1:15.5 ratio of secondary alcohol–primary alcohol, together with a 1% content of impurity. Infrared spectral evidence indicated the latter to be a silicon hydride (sharp absorption at 2150 cm.$^{-1}$).

Column chromatography on Florisil and elution with 15% ethyl ether in petroleum ether (b.p. 30–60°) afforded the 1-(tri-*p*-tolylsilyl)ethanol. This was recrystallized from methanol and from *n*-hexane, m.p. 88–88.5°. Its infrared spectrum displayed a characteristic absorption at 880 cm.$^{-1}$. Furthermore, t melted depressed when admixed with the primary alcohol.

Further chromatographic elution with ethyl ether yielded the 2-(tri-*p*-tolylsilyl)ethanol. Recrystallization from *n*-hexane resulted in a product melting at 90–91°. An n.m.r. spectrum displayed the high- and low-field triplets, together with intervening singlet hydroxyl and methyl proton resonances.

G. **Epoxyethyltri-*p*-fluorophenylsilane.**—Gas chromatography of the crude reaction product on a 5% silicone gum rubber-on-firebrick column at various temperatures revealed only one component. To bolster the conclusion that only one alcohol was formed, the product was recrystallized from cyclohexane (m.p.

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[21] The authentic samples were synthesized by Mr. G. R. Husk of this laboratory in connection with a study of directive influences in aluminum hydride–olefin interactions. His assistance is gratefully acknowledged.

[22] In the case of secondary or 1-substituted ethanols arising in the ethyl, phenyl, and *p*-tolyl runs this structural type displayed an infrared absorption at 875–890 cm.$^{-1}$, while the primary or 2-substituted ethanols absorbed at 915–925 cm.$^{-1}$. The infrared spectral difference was useful in discerning small amounts of the secondary alcohol in the crude reduction product or in column chromatographic fractions.

[23] The authors wish to thank Professor Henry Gilman of Iowa State University for providing an authentic sample of this compound.

83–84°) and n.m.r. spectra obtained both for the pure primary alcohol and the residue of the mother liquor. There were no extraneous resonance signals indicating the presence of the secondary alcohol. The n.m.r. spectrum displayed the two triplets (in δ values) at 1.63 and 3.72.

H. Epoxyethyltris(*p*-trifluoromethylphenyl)silane.—The crude reduction product could not be analyzed quantitatively by gas chromatography due to the negative polarity ionization characteristics of the fluoro derivative. However, qualitatively the absence of olefin or starting epoxide could be confirmed, and the presence of a major and a very minor component could be detected. The crude product (3.42 g.) was introduced onto a Florisil column in a minimum amount of ethyl ether. The following eluents and fractions were employed: (1) petroleum ether (b.p. 30–60°), 0.07 g. of oil; (2) 10% ethyl ether in petroleum ether, 0.71 g. of solid; (3) fraction 2 eluent, 1.33 g. of solid; (4) fraction 2 eluent, 0.76 g. of solid; and (5) fraction 2 eluent, 0.08 g. of oil. Fraction 2 and 4 were recrystallized from cyclohexane individually (m.p. 120–121 and 102–103°, respectively) and submitted for elemental analysis. Fraction 2 gave satisfactory carbon and hydrogen values for a substituted ethanol, but the values for fraction 4 were 0.76% high on carbon and 0.52% high on hydrogen. The infrared spectra of fractions 2 and 4 were identical, except for a weak absorption at 1225 cm.$^{-1}$ in fraction 4. The n.m.r. spectra of both samples were consistent with the major constituent in both fractions being 2-tris(*p*-trifluoromethylphenyl)silane. Only two unexplained singlets of modest intensity in the n.m.r. spectrum of fraction 4 distinguished the spectra. It is, therefore, concluded that fraction 2 and 4 represent different crystal forms of the primary alcohol, the latter being somewhat impure, and that no secondary alcohol could be detected. The total yield of primary alcohol was estimated to be >90%.

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Notes

Chemistry of Alkali Metal–Unsaturated Hydrocarbon Adducts. V. Reductive Coupling of Vinylsilanes and the d_π–p_π Effect(1)

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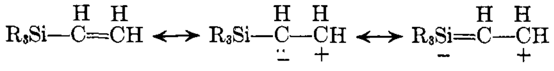
The ability of organic compounds containing carbon–carbon double bonds to form alkali metal adducts in ether solution has been associated with the presence of conjugated unsaturation. Arylethylenes and 1,3-butadienes readily form alkali metal addition compounds which can undergo subsequent dimerization or polymerization.(3) Typical of this behavior is the reaction of 1,1-diphenylethylene with metallic sodium in ether; hydrolysis of the resulting metal adduct yields 1,1,4,4-tetraphenylbutane.(4)

Accumulated physical and chemical evidence derived from vinylsilanes strongly supports the view that the available d-orbitals of silicon can interact with the π-electron cloud of the vinyl group (d_π–p_π effect), as shown in structures I–III.(5) Most recently, an infrared study of a series of vinylsilanes uncovered a correlation between the CH_2 out-of-plane deformation frequency of the vinyl group and electronic parameters of the group R.(6) This relation accords with a variation in the d_π–d_π interaction (III) as the electron-attracting character of the silicon is modified by its substituent R.



I II III

$$R_3Si—\overset{H}{C}=\overset{H}{C}H \longleftrightarrow R_3Si—\underset{\ddot{-}}{\overset{H}{C}}—\underset{+}{\overset{H}{C}}H \longleftrightarrow R_3Si=\underset{-}{\overset{H}{C}}—\underset{+}{\overset{H}{C}}H$$

The resemblance of such electronic effects to the conjugative delocalizations attainable in arylethylenes prompted an investigation of the ability of vinylsilanes to form alkali metal adducts. Although two recent investigations of alkali metal–arylsilane interactions by means of electron spin resonance spectroscopy have demonstrated the formation of radical-anion intermediates,(7) no such evidence has been obtained for the unconjugated olefinic linkage of vinylsilanes. The present study reports the facile reductive coupling of vinylsilanes by lithium metal and thereby presents strong chemical evidence in favor of the capacity of vinyl groups adjacent to silicon to yield reactive alkali metal adducts because of d_π–p_π delocalization. Thus, when triphenylvinylsilane in tetrahydrofuran solution was treated with one equivalent of lithium metal at −75°, a pale yellow precipitate was slowly deposited. Subsequent hydrolysis under mildly acidic conditions gave no discernible products of silicon–carbon bond cleavage,(8) but only starting material and a good yield of the reduction product V. The identity of V as 1,4-bis(triphenylsilyl)butane was established by its un-

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(1) Previous papers in this series: (a) J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28**, 2145 (1963); (b) J. J. Eisch, *ibid.*, **28**, 707 (1963); (c) J. J. Eisch and R. M. Thompson, *ibid.*, **27**, 4171 (1962); and (d) J. J. Eisch and W. C. Kaska, *ibid.*, **27**, 3745 (1962).

(2) (a) To whom inquires should be addressed at the Department of Chemistry, Catholic University of America, Washington 17, D. C.; (b) Undergraduate Research Participant, National Science Foundation, 1962–1963.

(3) G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 27–42.

(4) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 477 (1914).

(5) C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp. 91–113.

(6) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487 (1963).

(7) (a) M. G. Townsend, *J. Chem. Soc.*, 51 (1963); (b) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Am. Chem. Soc.*, **85**, 822 (1963).

(8) If silicon–carbon bond cleavage had occurred, the resulting silyllithium compound, R_3SiLi, would be expected to produce either R_3SiH or its hydrolysis products, R_3SiOH and R_3Si-O-SiR_3, upon treatment with water [*cf.* D. Wittenberg and H. Gilman, *Quart. Rev.*, **13**, 116 (1959)].