Organosilicon Compounds with Functional Groups Proximate to Silicon. 13. Cleavage and Rearrangement Reactions of Epoxyethylsilanes[1]

John J. Eisch* and James E. Galle

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

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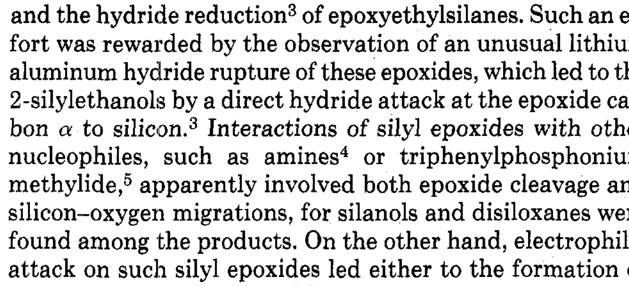
Acid- and base-promoted cleavage and rearrangement processes of the following epoxides were examined: epoxyethyl(triphenyl)silane (**2a**), *cis*-α,β-dideuterioepoxyethyl(triphenyl)silane (**2b**), α-deuterioepoxyethyl(triphenyl)silane (**2c**), and the cis and trans isomers of β-trimethylsilylstyrene oxide (**5a** and **5b**). As nucleophiles, phenyllithium, benzylamine, piperidine and morpholine and diisobutylaluminum hydride or deuteride and, as electrophiles, magnesium bromide and hydrogen chloride were evaluated. The thermal reactions of the epoxides **2a** and **2c** and the intermediate ring-opened epoxide cleavage products were studied. In general, the nucleophiles attacked preferentially the epoxide carbon α to the silicon in **2** and **5**, either directly with the subsequent loss of R_3SiOH or indirectly via a carbenoid intermediate with the subsequent loss of Li_2O. Phenyllithium reacted with **2a** to form styrene and $(C_6H_5)_4Si$; **2b** gave a 1:1 mixture of *cis*- and *trans*-α,β-dideuteriostyrene; and **2c** gave α-deuteriostyrene. Diisobutylaluminum deuteride and **2a** yielded only β-deuterio-β-triphenylsilylethanol. Electrophiles tended to give products arising from both modes of epoxide ring cleavage. **2a** with HCl yielded β-triphenylsilylacetaldehyde, β-chloro-α-triphenylsilylethanol, and chloro(triphenyl)silane. Magnesium bromide and **2a** gave the aldehyde with ca. equal distribution of the deuteron between C_1 and C_2. Finally, pyrolysis of **2c** at 275 °C gave the triphenyl(vinyloxy)silane with 60% of the deuteron β-cis to the silicon, 20% β-trans, and 20% α to silicon. The foregoing cleavage, elimination, and rearrangements are unified by polar mechanistic paths, some of whose intermediates have been subjected to trapping and stereochemical tests.

Curiosity as to how a triorganosilyl substituent would influence the reactivity and mode of cleavage of an adjacent epoxide group prompted our original studies on the synthesis[2] and the hydride reduction[3] of epoxyethylsilanes. Such an effort was rewarded by the observation of an unusual lithium aluminum hydride rupture of these epoxides, which led to the 2-silylethanols by a direct hydride attack at the epoxide carbon α to silicon.[3] Interactions of silyl epoxides with other nucleophiles, such as amines[4] or triphenylphosphonium methylide,[5] apparently involved both epoxide cleavage and silicon–oxygen migrations, for silanols and disiloxanes were found among the products. On the other hand, electrophilic attack on such silyl epoxides led either to the formation of β-silylcarbonyl derivatives[3,6] or, by protodesilylation, to silicon-free carbonyl derivatives.[7] In fact, this latter mode of cleavage is basic to the recent use of epoxyalkylsilanes as carbonyl precursors in novel organic syntheses.[8]

Therefore, we were encouraged to undertake a more extensive survey of the acid- and base-promoted cleavages of epoxyethylsilanes. To permit monitoring of the regiochemistry or stereochemistry involved in such cleavages, reaction was conducted not only on epoxyethyl(triphenyl)silane (**2a**), but also on *cis*-α,β-dideuterioepoxyethyl(triphenyl)silane (**2b**), α-deuterioepoxyethyl(triphenyl)silane (**2c**), and the cis and trans isomers of β-trimethylsilylstyrene oxide (**5a** and **5b**), all of which were prepared by the epoxidation of the corresponding vinylsilanes (eq 1).



(1)

1a, $R = C_6H_5$; A, B, X = H
b, $R = C_6H_5$; A, B = D; X = H
c, $R = C_6H_5$; A = D; B, X = H

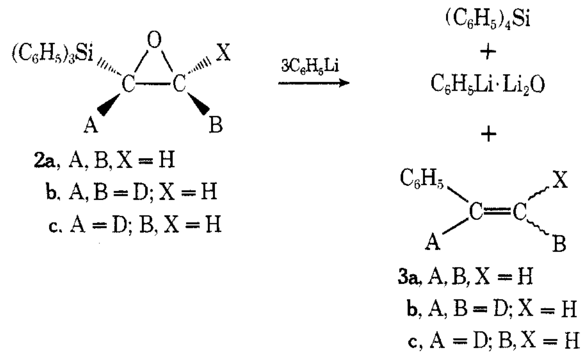
2a, $R = C_6H_5$; A, B, X = H
2b, $R = C_6H_5$; A, B = D; X = H
2c, $R = C_6H_5$; A = D; B, X = H
5a, $R = CH_3$; A, B = H; X = C_6H_5
5b, $R = CH_3$; A, X = H; B = C_6H_5

In the following report we shall describe reaction pathways for the cleavage of these epoxides by, in turn, phenyllithium, primary and secondary amines, dialkylaluminum hydride, and hydrogen chloride. Certain of these reactions will be compared with recently published preliminary reports on the thermal rearrangements[9] and organocuprate cleavages[10] of silyl epoxides, in order to arrive at a unified mechanistic view of epoxyalkylsilane chemistry.

Results

Cleavage by Phenyllithium. Epoxyethyl(triphenyl)silane (**2a**) with phenyllithium in ether at 0 °C formed styrene and tetraphenylsilane. One equivalent of **2a** required ca. 3 equiv of phenyllithium. Thus, when equimolar amounts of **2a** and the lithium reagent were admixed, the isolated yields of pure tetraphenylsilane realized were 23–27% with material balances of 91–94%. Lithium bromide present in the phenyllithium solution did not play a role in this reaction (possibly by inducing a rearrangement of **2a**).[3,6] The reaction of **2a** with lithium halide free phenyllithium[11] gave identical results.

To learn at which carbon of epoxide **2a** the attachment of phenyllithium occurred, the α-deuterated epoxide **2c** was subjected to cleavage. The styrene formed in 86% yield was shown by NMR analysis to be exclusively α-deuteriostyrene (**3c**), and thus the phenyllithium had ultimately attacked the carbon α to silicon in **2c** (eq 2).



(2)

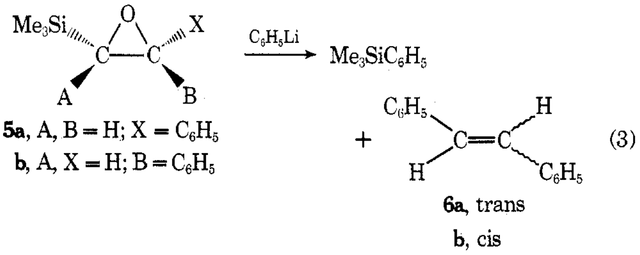
2a, A, B, X = H
b, A, B = D; X = H
c, A = D; B, X = H

3a, A, B, X = H
b, A, B = D; X = H
c, A = D; B, X = H

A corresponding reaction of **2b** with phenyllithium established that the formation of styrene was nonstereospecific; the α,β-dideuteriostyrene (**3b**) was a 1:1 mixture of the cis and trans isomers.

From the observed stoichiometry of eq 2, it would seem that the lithium oxide thus formed might be responsible for complexing with and thereby deactivating 1 equiv of the phenyllithium employed.[12]

Both *cis*- and *trans*-β-trimethylsilylstyrene oxides gave ca. 95% of *trans*-stilbene and traces of *cis*-stilbene, together with trimethyl(phenyl)silane (eq 3).

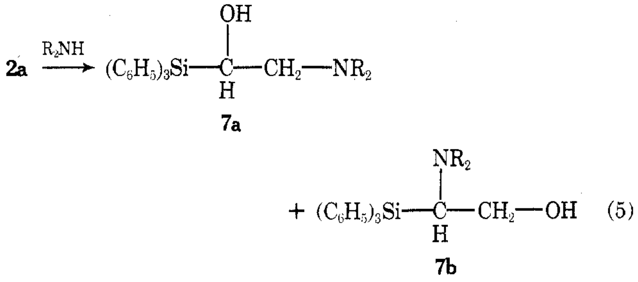

5a, A, B = H; X = C_6H_5
b, A, X = H; B = C_6H_5
6a, trans
b, cis
(3)

To learn if the olefin formation in eq 2 and 3 might result from the elimination of lithium triorganosilanolate (cf. infra), such a salt was treated with phenyllithium under the same conditions. However, treatment of triphenylsilanol (**4a**) with 4 equiv of phenyllithium in diethyl ether gave only traces of tetraphenylsilane, with the latter undoubtedly arising by way of hexaphenyldisiloxane (eq 4).

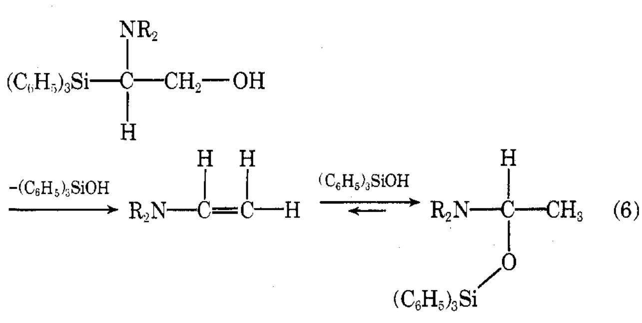
$$\underset{\mathbf{4a}}{(C_6H_5)_3Si\text{—}OH} \xrightarrow[\quad]{C_6H_5Li}\!\!\!\!\!\!/\;\; (C_6H_5)_4Si \xleftarrow{C_6H_5Li} (C_6H_5)_3Si\text{—}O\text{—}Si(C_6H_5)_3 \quad (4)$$

No intermediates could be detected in the reaction of epoxide **2a** with phenyllithium at low temperatures: at −78 °C no reaction occurred, and at −23 °C only styrene and tetraphenylsilane were formed. The absence of triphenylsilanol in this low-temperature reaction and its failure to undergo efficient conversion to tetraphenylsilane by phenyllithium (eq 4) argue against its being an intermediate in eq 2.

Cleavage by Primary and Secondary Amines. Epoxyethyl(triphenyl)silane (**2a**) with benzylamine, piperidine, or morpholine at 110–155 °C formed triphenylsilanol (**4a**) and hexaphenyldisiloxane (**12**). Isolation of intermediates by conducting the reaction under milder conditions proved to be impossible, but their detection by NMR monitoring was informative. Although no new peaks were observed, whose chemical shifts would be consonant with the simple adducts (eq 5), new doublet peaks at high field (0.8–1.6 ppm) appeared, whose origin could be ascribed to the rearrangement product of the latter intermediate (**7b**), as in eq 6. The enamine intermediate could undergo polymerization under the reaction conditions, thus preventing the detection of acetaldehyde when the reaction mixture was treated with an acidified 2,4-dinitrophenylhydrazine solution. That the silanol **4a** (disiloxane **12**) was formed furnishes indirect evidence for the preferred formation of adduct **7b**, for only this adduct would be expected to have a facile pathway leading to the loss of triphenylsilanol (cf. eq 6). As to the origin of the disiloxane **12**, it is known that heating **4a** in basic solvents leads to the formation of **12**.[13]



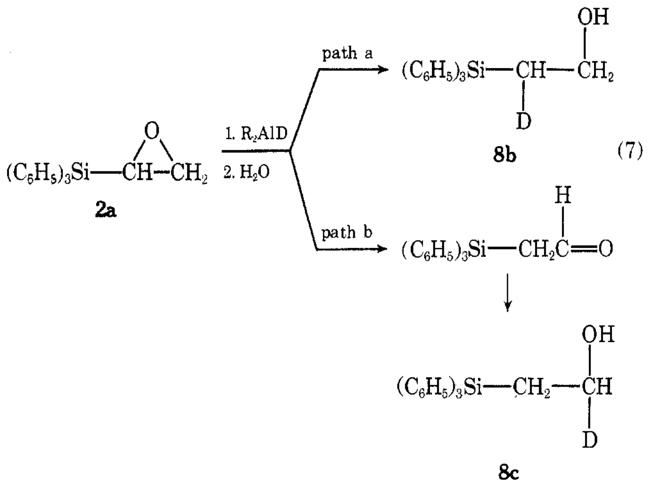
$$\mathbf{2a} \xrightarrow{R_2NH} \underset{\mathbf{7a}}{(C_6H_5)_3Si\text{—}\overset{OH}{\underset{H}{C}}\text{—}CH_2\text{—}NR_2} + \underset{\mathbf{7b}}{(C_6H_5)_3Si\text{—}\overset{NR_2}{\underset{H}{C}}\text{—}CH_2\text{—}OH} \quad (5)$$



$$(C_6H_5)_3Si\text{—}\overset{NR_2}{\underset{H}{C}}\text{—}CH_2\text{—}OH \xrightarrow{-(C_6H_5)_3SiOH} R_2N\text{—}\overset{H}{C}\text{=}\overset{H}{C}\text{—}H \xrightleftharpoons{(C_6H_5)_3SiOH} R_2N\text{—}\overset{H}{\underset{O\text{—}Si(C_6H_5)_3}{C}}\text{—}CH_3 \quad (6)$$

The behavior of the less reactive *cis*-β-trimethylsilylstyrene oxide (**5a**) with benzylamine tends to support the foregoing description of such cleavages. An NMR monitoring of the early stages of reaction did reveal doublets of equal intensity whose chemical shifts (4.47 and 2.12 ppm) are consonant with presence of the intermediate, $C_6H_5CHOHCHNR_2SiMe_3$, in solution.

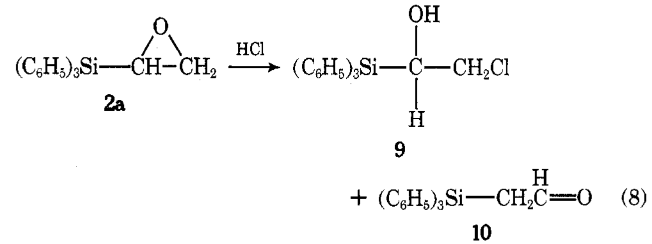
Cleavage by Dialkylaluminum Hydride. Although lithium aluminum hydride has already been shown to attack **2a** by direct hydride attack at the carbon α to silicon,[3] it was interesting to learn how an electrophilic hydride reagent like diisobutylaluminum hydride would behave. Treatment of **2a** with this hydride in hexane gave rapid reduction and a high yield of β-triphenylsilylethanol (**8a**). To learn whether direct reduction (path a) or reduction with preliminary rearrangement (path b) took place (eq 7), the reduction of **2a** was repeated with diisobutylaluminum deuteride.



$$\underset{\mathbf{2a}}{(C_6H_5)_3Si\text{—}\overset{O}{CH\text{—}CH_2}} \xrightarrow[2.\ H_2O]{1.\ R_2AlD} \begin{cases} \xrightarrow{\text{path a}} \underset{\mathbf{8b}}{(C_6H_5)_3Si\text{—}\underset{D}{CH}\text{—}\overset{OH}{CH_2}} \\ \xrightarrow{\text{path b}} (C_6H_5)_3Si\text{—}CH_2\overset{H}{C}\text{=}O \longrightarrow \underset{\mathbf{8c}}{(C_6H_5)_3Si\text{—}CH_2\text{—}\overset{OH}{\underset{D}{CH}}} \end{cases} \quad (7)$$

However, an NMR analysis of the product and comparison with an authentic sample[3] demonstrated that only **8b** was formed.

Cleavage with Hydrogen Chloride. Epoxyethyl(triphenyl)silane with anhydrous hydrogen chloride in benzene gave both epoxide cleavage and isomerization (eq 8).

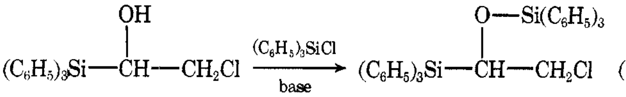


$$\underset{\mathbf{2a}}{(C_6H_5)_3Si\text{—}\overset{O}{CH\text{—}CH_2}} \xrightarrow{HCl} \underset{\mathbf{9}}{(C_6H_5)_3Si\text{—}\overset{OH}{\underset{H}{C}}\text{—}CH_2Cl} + \underset{\mathbf{10}}{(C_6H_5)_3Si\text{—}CH_2\overset{H}{C}\text{=}O} \quad (8)$$

The structure of **9** was established by means of the lanthanide shift reagent, Eu(fod)$_3$,[14] which caused the one-proton packet of **9** to be shifted downfield to the greatest extent.

Chloro(triphenyl)silane was also formed in the course of this reaction, either by the dissociation of **9** into acetaldehyde and this chlorosilane or directly from **16** (cf. eq 13 and 14). This point was established by heating purified **9** and trapping the evolved acetaldehyde in a solution of 2,4-dinitrophenylhydrazine.

Because of the presence of chloro(triphenyl)silane in the original reaction mixture, workup with alkaline reagents led to the formation of β-triphenylsiloxy-β-triphenylsilylethyl chloride (**11**), which was shown to arise from the action of the chlorosilane on **9**.



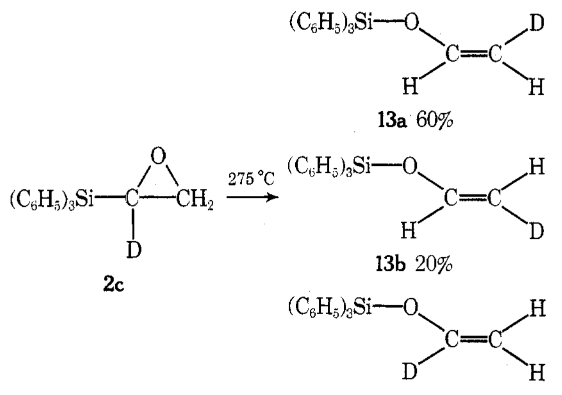
$$(C_6H_5)_3Si\text{—}\overset{OH}{CH}\text{—}CH_2Cl \xrightarrow[\text{base}]{(C_6H_5)_3SiCl} (C_6H_5)_3Si\text{—}\overset{O\text{—}Si(C_6H_5)_3}{CH}\text{—}CH_2Cl \quad (9)$$

9 **11**

Rearrangements of Epoxyethyl(triphenyl)silane. In the midst of our studies on the thermal rearrangements of epoxyalkylsilanes, a preliminary report of a very comprehensive study appeared.[9] Hence, we shall restrict ourselves to mentioning only our complementary findings.

For our thermal isomerizations of **2a** in the liquid phase there was some indication that traces of acid remaining on the glassware catalyzed the isomerization of **2a** to triphenyl(vinyloxy)silane. Isomerizations conducted with carefully rinsed glassware were slower. The presence of air or hydroquinone retarded the reaction as well.

Isomerization of the α-deuterio isomer **2c** at 275 °C led to the formation of principally (ca. 80%) the β-deuteriovinyloxysilanes, **13a** and **13b**, in a 3:1 ratio and probably 20% of the α-deuterio isomer, **13c**.



13a 60%

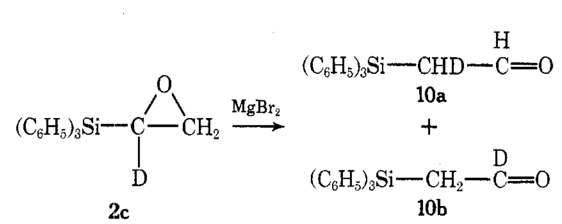
13b 20%

13c 20%

2c

(10)

The magnesium bromide catalyzed isomerization of **2c** to the aldehyde **10** was also undertaken, in order to learn what the deuterium label would reveal about the reaction course. Treatment of **2c** with magnesium bromide led to an equimolar mixture of 1- and 2-deuterated isomer of **10**.



10a

10b

2c

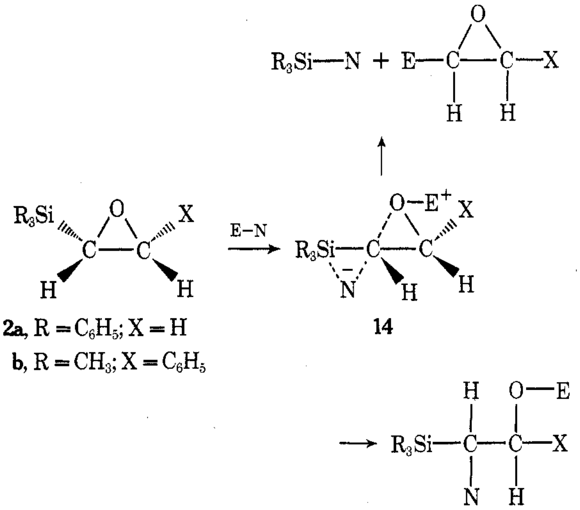
(11)

Discussion

Three aspects of epoxyalkylsilane chemistry deserve general consideration, namely the regiochemistry of epoxide ring opening, the ensuing desilylative elimination reactions of such ring-opened adducts, and the attendant rearrangement processes of both epoxides and their reaction intermediates.

Regiochemistry of Epoxide Opening. In the foregoing reactions of epoxyethylsilanes (**2a, 5a,** and **5b**) with phenyllithium or with diisobutylaluminum hydride, attack of these reagents was shown to be indisputably regiospecific for the epoxide carbon α to the silicon. The same regiospecificity most probably also obtains for the rupture of epoxides **2a** and **5a** by primary or secondary amines (eq 5 and 6). Attack of these amines preferentially at the epoxide carbon α to silicon (giving adducts of type **7b**) is indirectly proved, for only such adducts could easily permit the ready, observed elimination of the triorganosilanol (eq 6). However, the formation of $R_3SiC_6H_5$, rather than R_3SiOH, in the reactions of epoxides **2** and **5** with phenyllithium reveals an unusual feature of such interactions.

These results can be incorporated into a generalized view of nucleophilic attack on epoxyalkylsilanes, which has already been adumbrated in discussing the lithium aluminum hydride opening of such epoxides.[3] Nucleophilic attack can be viewed as proceeding through a three-centered transition state **14**, which can lead to rupture of the carbon–oxygen bond with assistance by some Lewis acid (E = Li^+, R_2AlH, $H \cdots NR_2$) or which can give rise to direct nucleophilic attack on silicon with the displacement of the epoxide ion (eq 12).



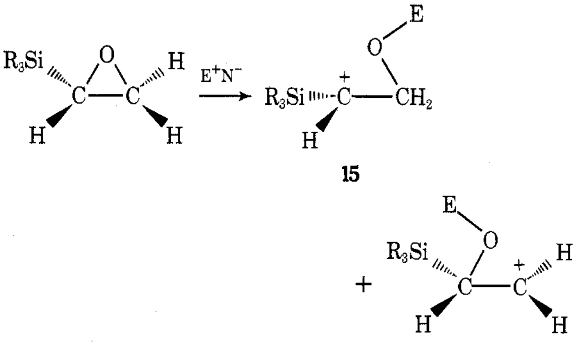
2a, R = C_6H_5; X = H
b, R = CH_3; X = C_6H_5

14

(12)

Nucleophilic attack on the carbon α to silicon (cf. **14**) is considered to be favored by simultaneous interaction of the approaching electron pair with the antibonding orbital on the epoxide carbon and the vacant 3d orbitals of silicon.

Where the nucleophilicity of the reagent is low, ring opening would be expected to be governed by the relative stability of the incipient carbonium ions generated by electrophile E^+ (eq 13).

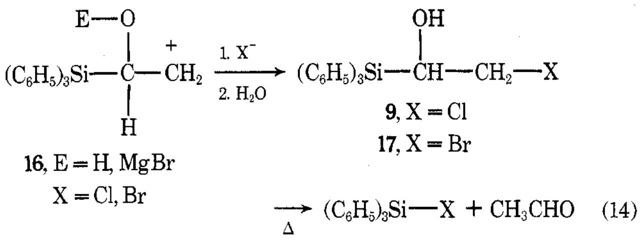


15

16

(13)

As judged by electronegativities (X_{Si} = 1.8 vs. X_H = 2.1), the transition state leading to **15** should be of lower energy. This view seems to accommodate nicely the behavior of epoxide **2a** toward magnesium bromide or hydrogen chloride. In both reactions products are formed that can be ascribed as arising via both intermediates **15** and **16**. With hydrogen chloride, the formation of β-triphenylsilylacetaldehyde (**10**) can be viewed as stemming from **15** via a hydride shift, while the chlorohydrin **9** would result by the capture of **16** with the chlorine ion (eq 8). With magnesium bromide, it is known that **2a** gives principally the acetaldehyde **10** (75% yield); this supports the above assumption that **15** is formed via a lower energy pathway. Although no bromohydrin **17** (analogous to chlorohydrin **9**) has been isolated from this reaction, variable amounts of triphenylsilanol have been detected.[3,4] Most likely this silanol results from the hydrolysis of bromo(triphenyl)silane, which in turn arises from the decomposition of *β*-bromo-*α*-triphenylsilylethanol. The latter intermediate would represent the capture product of **16** by bromide ion and would be expected to be even more prone to *β*-elimination than **9**[15] (eq 14).



$$(C_6H_5)_3Si-\underset{H}{\overset{\overset{+}{E-O}}{C}}-CH_2 \xrightarrow[2.\ H_2O]{1.\ X^-} (C_6H_5)_3Si-\overset{OH}{CH}-CH_2-X \xrightarrow[\Delta]{} (C_6H_5)_3Si-X + CH_3CHO \quad (14)$$

16, E = H, MgBr
X = Cl, Br

9, X = Cl
17, X = Br

Although this explanation of epoxide opening by electrophiles fits most of the facts, the subsequent discussion of rearrangements will address subtle complexities in these reactions.

Desilylative Eliminations. *β*-Eliminations of halohydrins **9** and **17** have been intensively studied.[15] Since it is known that *β*-silylalkanols undergo base-promoted elimination of triorganosilanol[10,16,17] it was initially believed that the interaction of phenyllithium with both epoxides **2a** and **5a** led to a *β*-silylethanol, which then underwent desiloxylation (path a).

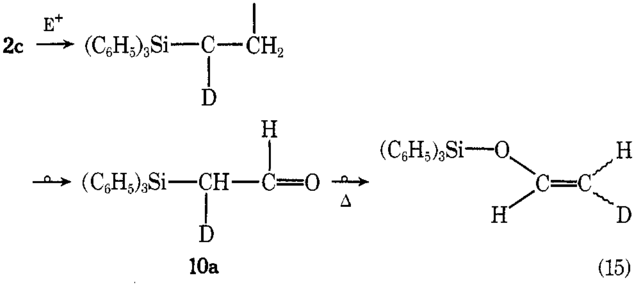
However, the nonstereospecificity in the olefins formed [1:1 mixture of *cis*- and *trans*-dideuteriostyrenes from **2b** (eq 2) and >95% *trans*-stilbene from **5a** or **5b** (eq 3)] is not in accord with path a, which elimination is stereospecific.[17] Nor can the observed formation of $R_3Si-C_6H_5$ be reconciled with this path: even if R_3SiOH were eliminated, it has been shown not to yield significant amounts of $R_3Si-C_6H_5$ with phenyllithium under the reaction conditions. Path b suffers disadvantages similar to path a. Only if **20** were to react more rapidly with phenyllithium to yield **23** than undergo direct elimination to provide **24** would this mechanism fit the facts. However, that **20** should undergo exclusively an intermolecular reaction to yield **23** and undergo no trace of intramolecular decomposition to **24** and R_3SiO^- seems highly unlikely. Hence, an alternative path must be sought.

Only a direct nucleophilic attack of phenyllithium on silicon, with the formation of the epoxide anion (**21**, path c), does offer a suitable route to $R_3Si-C_6H_5$ and **24**. Such an anion would be expected to yield a carbenoid **22** by *α*-elimination[18] and **23** would be formed by the trapping of **22** by phenyllithium. Loss of Li_2O by **23** would then yield the olefin **24** in a nonstereospecific fashion.

The elimination of R_3SiOH in the reactions of these epoxides with primary or secondary amines most likely occurs in a fashion analogous to path a in Scheme I, with intermediates such as **7b** undergoing silicon–oxygen interaction and elimination.

Rearrangements. In contrast to the retro-Wittig rearrangements[19] encountered in the foregoing epoxide reactions with nucleophiles, the electrophile-catalyzed rearrangement of *α*-deuterioepoxyethyl(triphenyl)silane led to isomeric aldehydes **10a** and **10b** (eq 11). The finding of ca. equal distribution of the deuteron between C_1 and C_2 forces one not only to postulate a hydride shift in **15** to account for **10,** but also to invoke a migration of R_3Si in intermediate **16** from one carbon to another. Such acid-catalyzed 1,2-silyl groups shifts have previously been reported.[20]

The unusual thermal rearrangement of this epoxide **2** reported in this study is similar to those recently described by Brook and co-workers.[9] From our limited data, we are inclined to believe that this reaction is acid catalyzed and may proceed via the formation of *β*-triphenylsilylacetaldehyde (**10**), which is known to rearrange readily to triphenyl(vinyloxy)silane.[6]

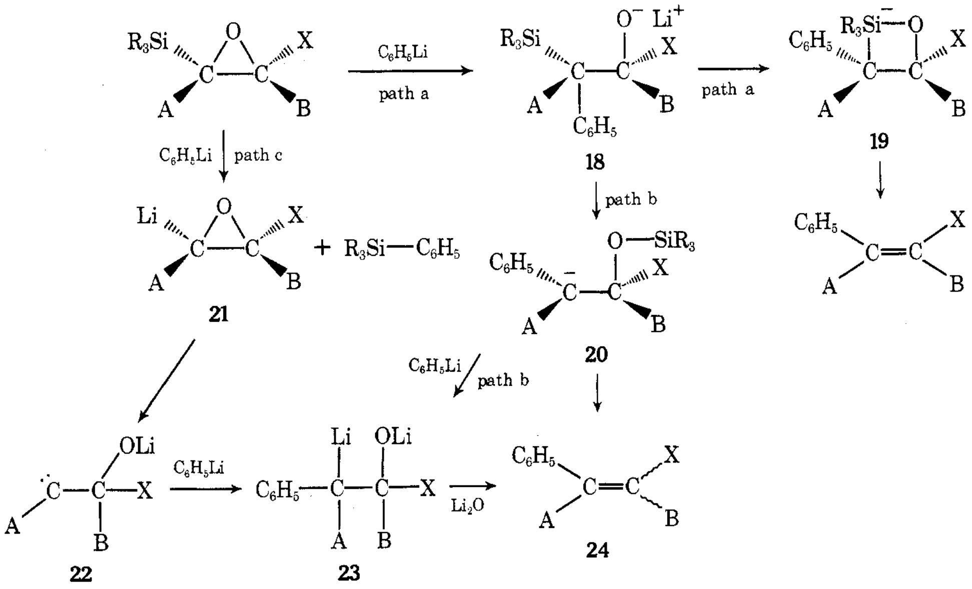


$$2c \xrightarrow{E^+} (C_6H_5)_3Si-\underset{D}{\overset{O-E}{C}}-CH_2 \longrightarrow (C_6H_5)_3Si-\underset{D}{CH}-\overset{H}{C}=O \xrightarrow[\Delta]{} \underset{H}{\overset{(C_6H_5)_3Si-O}{C}}=\underset{D}{\overset{H}{C}} \quad (15)$$

10a

Although such a rationale accounts for some of the facts, the stereoselective formation of **13a** is puzzling. Extensive studies to learn about the possible role of adventitious catalysts or surface reactions remain to be carried out.

Scheme I



Experimental Section

Melting points were determined with a Thomas-Hoover Unimelt apparatus and are corrected. Infrared spectra were recorded of samples as potassium bromide disks, mineral oil suspensions, or solutions in pure solvents by means of a Perkin-Elmer spectrophotometer, Model 457. Proton magnetic resonance spectra were recorded with Varian spectrometers, either a Model A-60 or a Model HA-100D, the latter being equipped with a proton and deuterium decoupler (Model HP-205AG). Such NMR data are presented on the δ scale in parts per million relative to tetramethylsilane, followed by the integrated intensities and the coupling constants in hertz. Mass spectra were obtained with a Du Pont spectrometer, Model 21-491BR, equipped for the gas chromatographic introduction of samples. Separate gas chromatographic analyses were performed with an F & M instrument, Model 720, equipped with dual columns of 10% silicone gum rubber on 60–80 mesh Chromosorb W. Elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

All reactions of the epoxides with organometallic compounds or other cleavage reagents were conducted under an atmosphere of dry nitrogen and in anhydrous solvents.

Starting Materials. Triphenyl(vinyl)silane (**1a**),[2] ethynyl(triphenyl)silane,[21] trimethyl[(*E*)-β-styryl]silane,[22] and trimethyl[(*Z*)-β-styryl]silane[22] were prepared and purified according to published procedures. Epoxyethyl(triphenyl)silane (**2a**) was prepared by the epoxidation of triphenyl(vinyl)silane either with peroxytrifluoroacetic acid[3] or with *m*-chloroperbenzoic acid (cf. infra).

cis-β-Trimethylsilylstyrene oxide (**5a**) and *trans*-β-trimethylsilylstyrene oxide (**5b**) were prepared from the corresponding trimethyl(β-styryl)silanes by adding dropwise a solution of 40 mmol of the styrylsilane in 20 ml of chloroform to 44 mmol of *m*-chloroperbenzoic acid (85% pure) in 90 ml of chloroform cooled to 0 °C. After the addition, the solution was stirred at 20–25 °C for 48 h. The resulting white suspension was taken up in benzene and the solution then extracted, in turn, with aqueous sodium bicarbonate, aqueous sodium bisulfite, and aqueous sodium bicarbonate solutions. Drying the benzene layer over anhydrous sodium sulfate, solvent removal, and distillation gave the epoxides: (1) cis isomer **5a**, bp 55–59 °C (0.5 mm), 65% yield (>95% pure by NMR and GC, but may rearrange without detection on GC; cf. infra), NMR (CCl$_4$) δ 0.20 (s, 9), 2.77 (d, 1, J = 5.5 Hz), 4.52 (d, 1, J = 5.5 Hz), and 7.65 (s, 5); (2) trans isomer **5b**, bp 60–62 °C (0.5 mm), 70% yield (>95% pure by NMR, but underwent rearrangement on GC with inlet at 270 °C) after purification by chromatography on a Florisil column with a hexane elution, NMR (CCl$_4$) δ 0.49 (s, 9), 2.53 (d, 1, J = 3.2 Hz), 3.97 (d, 1, J = 3.2 Hz), and 7.54 (s, 5).[9,23]

***cis*-α,β-Dideuteriovinyl(triphenyl)silane (1b).** A solution of ethynyl(triphenyl)silane[21] (9.88 g, 34.8 mmol) and anhydrous *N*-methylpyrrolidine (4.68 g, 55 mmol) in 100 ml of hexane was cooled to −78 °C and slowly treated with diisobutylaluminum deuteride (7.87 g, 55 mmol, ca. 95% pure). The mixture was allowed to attain room temperature slowly and then was heated at reflux for 25 h. The solution was cooled and cautiously treated with 13 ml of deuterium oxide (99.9%). The separated organic product was brought into solution with methylene chloride. The organic extract was dried over anhydrous magnesium sulfate and the solvent then removed. Column chromatography on Florisil in the published manner and recrystallization from 95% ethanol gave an adequately pure product, mp 60–61 °C, in low yield, since contaminants were difficult to remove: NMR (CDCl$_3$) δ 5.70 (t, 1, J = 3 Hz) and 7.0–7.6 (m, 15).

α-Deuteriovinyl(triphenyl)silane (1c). α-Deuteriovinyl chloride[24] was prepared from 2-bromo-1,1-dichloro-1-deuterioethane (11.5 g, 64 mmol) and dried thoroughly by vaporizing it successively through columns packed with phosphorus pentoxide and calcium hydride, respectively. The gas thus dried was passed into a flask containing a stirred mixture of magnesium turnings (1.20 g, 49 mmol) in 25 ml of dry tetrahydrofuran.[25] A cold-finger condenser charged with solid carbon dioxide and acetone was used to retain the vinyl chloride in the flask. After the Grignard reagent had formed, chloro(triphenyl)silane (10.5 g, 35 mmol) in 50 ml of tetrahydrofuran was added and the solution heated at reflux for 24 h. Usual workup gave 8.0 g (43%) of pure product: mp 69–70 °C; NMR (CDCl$_3$) δ 5.70 (ca. sextet, 1, $J \simeq$ 3 Hz), 6.13 (m, 1), and 7.0–7.6 (m, 15).

α-Deuterioepoxyethyl(triphenyl)silane (2c) and *cis*-α,β-Dideuterioepoxyethyl(triphenyl)silane (2b). A solution of **1c** (5.86 g, 19 mmol) and *m*-chloroperbenzoic acid (85%, 5.3 g, 26 mmol) in 30 ml of chloroform was allowed to stand at 20–25 °C for 24 h. The solidified mixture was dissolved in benzene and the resulting solution washed several times with 5% aqueous sodium bicarbonate, 5% aqueous sodium bisulfite, and again with the bicarbonate solution. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed. Column chromatography on Florisil gave 1.27 g of recovered **1c** and 4.35 g of the epoxide **2c** (94% yield). Recrystallized from a 95% ethanol–methylene chloride pair, **2c** melted at 85–86 °C: NMR (CDCl$_3$) δ 2.43 (d, 1, J = 5 Hz), 2.81 (d, 1, J = 5 Hz), and 6.9–7.6 (m, 15).

In a similar manner, **1b** was converted to epoxide **2b**: NMR (CDCl$_3$) δ 2.41 (br, s, 1) and 6.9–7.6 (m, 15).

Reaction of Epoxyethyl(triphenyl)silanes with Phenyllithium. A. Epoxyethyl(triphenyl)silane.[4] When 1.50 g (5 mmol) of **2a** in 50 ml of anhydrous diethyl ether was treated at 0 °C with 4.3 mmol of phenyllithium in 25 ml of ether for 45 min, subsequent hydrolysis and separation of the ether layer led to the detection of styrene, tetraphenylsilane (27%, mp 225–228°C), and recovered **2a** (64%, mp 68–72 °C).

A similar run allowed to react at 20–25 °C for 20 h gave a 23% yield of tetraphenylsilane (mixture melting point and ir spectrum) and a 71% recovery of **2a.**

An 88-mg sample of **2a** (2.9 mmol) in 30 ml of dry ether was titrated at 0 °C with an ethereal solution of 12.6 mmol of phenyllithium until the Gilman Michler's ketone color test on an aliquot just turned permanently positive. Upon the basis of a simple acid–base assay of the phenyllithium, this titration indicated that ca. 4 equiv of the lithium reagent was required per mole of **2a.** That this value was high was shown by adding 0.16 mmol of **2a** to turn the Gilman test negative and by treating the solution with solid carbon dioxide. Benzene and aqueous potassium hydroxide were then added and the benzene layer reextracted with more base, dried over anhydrous magnesium sulfate, and stripped of solvent and biphenyl. The resulting residue was essentially pure tetraphenylsilane, 1.0 g (96%), mp 233–236 °C after recrystallization from cyclohexane.

The aqueous layer yielded 0.32 g of benzoic acid upon acidification. Since this accounts for 2.6 mmol of the phenyllithium employed, 10 mmol of the lithium reagent had reacted with 3.1 mmol of **2a.**

B. α-Deuterioepoxyethyl(triphenyl)silane (2c). A solution of 1.66 g of **2c** (5.4 mmol) in 15 ml of diethyl ether was rapidly treated at 20–25 °C with 16.2 ml of 1.0 M phenyllithium in ether. After a 2-min period 2 ml of water was cautiously added. The precipitated tetraphenylsilane was dissolved by the addition of methylene chloride and the resulting solution dried over anhydrous magnesium sulfate. The solvents were removed at 25 °C under 20 mm pressure and then the styrene was condensed into a dry ice cooled trap by heating at 50 °C under 0.1 mm pressure. An NMR analysis showed that only α-deuteriostyrene (500 mg, 86%) was present. The nonvolatile residue was essentially pure tetraphenylsilane, 1.52 g (83%), mp 233–237 °C, after recrystallizations from a 95% ethanol–methylene chloride pair.

C. *cis*-α,β-Dideuterioepoxyethyl(triphenyl)silane (2b). A similar reaction was carried out with **2b** and phenyllithium. The styrene isolated and purified twice by GC collection was shown by NMR spectral analysis to be a mixture of *cis*- and *trans*-dideuteriostyrene: relative integrated intensities of aromatic:cis-β:trans-β protons 5.0:0.5:0.5 (±0.1).

D. Search for Intermediates. Treatment of 1.0 mmol of **2a** in 10 ml of ethyl ether with 4.2 mmol of phenyllithium in 4 ml of ether at −78 °C (dry ice–acetone bath) gave no reaction after 2 h.

An analogous reaction at −23 °C (dry ice–CCl$_4$ bath) led to a precipitate of tetraphenylsilane after a few minutes. Hydrolysis after 30 min at −23 °C and usual workup revealed the presence of only styrene, tetraphenylsilane, and **2a.** Specifically, no triphenylsilanol could be detected.

E. Control Reaction of Triphenylsilanol with Phenyllithium. Treatment of 1.104 g (4 mmol) of **4a** in 20 ml of ethyl ether with 16 ml (16.8 mmol) of ethereal phenyllithium over a period of 2 h at 25 °C gave a homogeneous solution. After 15 min hydrolysis and usual workup gave only 57 mg (4%) of tetraphenylsilane; the rest was recovered **4a.**

Reaction of the β-Trimethylsilylstyrene Oxides with Phenyllithium. A. Cis Isomer (5a).[23] A solution of 1.45 g (7.5 mmol) of **5a** (96% pure) in 20 ml of anhydrous diethyl ether was treated with 24 mmol of phenyllithium in ether, whereupon a marked exotherm resulted. After 30 min the mixture was hydrolyzed cautiously. The separated organic layer was dried over anhydrous sodium sulfate and the volatile components were distilled off at normal pressure. The residue was shown by a combination of GC and NMR analysis to contain *trans*-stilbene (**6a**), only a trace of *cis*-stilbene (**6b**, <5%), trimethyl(phenyl)silane, and biphenyl. The *trans*-stilbene was isolated by recrystallization from methanol and identified; the silane was separated by volatilization from the residue at reduced pressure.

B. Trans Isomer (5b).[23] In a similar manner, 3 mmol of **5b** and 12 mmol of phenyllithium gave only the trans isomer of stilbene, together with trimethyl(phenyl)silane and biphenyl. The trans isomer was isolated and identified by mixture melting point and ir spectral comparisons.

Reaction of Epoxyethyl(triphenyl)silane (2a) with Diisobutylaluminum Hydride. To a stirred suspension of **2a** (604 mg, 2.0 mmol) in 10 ml of hexane was added 0.40 ml (2.2 mmol) of the hydride. The mixture became warm and homogeneous. After 1 h at 20–25 °C the solution was cooled and cautiously treated with 1.0 ml of water and then with 50 ml of methylene chloride. The solution was dried over anhydrous magnesium sulfate and then concentrated under reduced pressure. β-Triphenylsilylethanol (**7a**) separated from the concentrated solution in 83% yield (516 mg, mp 87–89 °C). Recrystallization from hexane gave a product, mp 99–100 °C, which by mixture melting point and ir spectra was identical with an authentic sample.[3]

The reaction of **2a** with diisobutylaluminum deuteride[26] was conducted in a similar manner. The product was shown to be exclusively β-deuterio-β-triphenylsilylethanol (**7b**) by comparison with an authentic sample.[3]

Reaction of Epoxyethyl(triphenyl)silane (2a) with Hydrogen Chloride. To an ice-cooled solution of **2a** (9.06 g, 30 mmol) in 60 ml of benzene was added, in one portion, 57 ml (30 mmol) of a 0.562 M solution of anhydrous hydrogen chloride in benzene. The solution was allowed to come to room temperature over 15 h. Removal of the solvent under reduced pressure gave a semisolid residue that was chromatographed on a Florisil column using an ether–hexane (1:9 v/v) eluent. The combined crystalline fractions were recrystallized from an ether–hexane pair to yield 5.25 g (51%) of product, which by NMR analysis was shown to contain ca. 80% of **9** and 20% of triphenylsilylacetaldehyde (**10**) (doublet at 2.97 and triplet at 9.61 ppm). Repeated recrystallization gave the pure chlorohydrin (**9**): mp 110–111 °C; NMR ($CDCl_3$) δ 2.20 (s, 1), 3.8–4.3 (m, 3), and 6.9–7.7 (m, 15).[4]

Anal. Calcd for $C_{20}H_{19}ClOSi$: C, 70.88; H, 5.65; Cl, 10.46. Found: C, 71.17; H, 5.54; Cl, 10.42.

Incremental additions of $Eu(fod)_3$ in a $CDCl_3$ solution of **9** and NMR spectral monitoring at 100 MHz caused the three-proton multiplet to resolve eventually into a one- and a two-proton packet. Since the one-proton packet was shifted the most by higher $Eu(fod)_3$ concentrations, the hydroxyl must be α to the silicon and the structure of **9** is then β-chloro-α-triphenylsilylethanol.

When the reaction of **2a** with hydrogen chloride was conducted as above, except that the benzene solution was stirred for 30 min with an excess of powdered, anhydrous sodium carbonate, subsequent workup yielded 20% of **9**, together with 30% of the triphenylsilyl ether of **9** (cf. infra). The isolation of this ether (**11**) demonstrated the presence of chlorotriphenylsilane in the reaction mixture.

β-Triphenylsiloxy-β-triphenylsilylethyl Chloride (11). A mixture of **9** (328 mg, 1.0 mmol), chlorotriphenylsilane (300 mg, 1.01 mmol), and anhydrous pyridine (120 mg, 1.51 mmol) was heated at reflux in 10 ml of hexane for 20 h. An additional 20 ml of hexane was used to aid a hot filtration of the suspension. Concentration and cooling of the filtrate gave 186 mg (31%) of the product, mp 138–140.5 °C. An analytical sample of **11** from cyclohexane melted at 143–144 °C and was shown to be identical with the product from the reaction of **1a** with hydrogen chloride.

Anal. Calcd for $C_{38}H_{33}ClOSi_2$ (597): C, 76.41; H, 5.56; C., 5.94. Found [mol wt (Rast), 590]: C, 76.01; H, 5.31; Cl, 5.94.

Thermal Decomposition of β-Chloro-α-triphenylsilylethanol and the Identification of Acetaldehyde. Under argon gas a sample of **9** (328 mg, 1 mmol) was gradually heated up to 200 °C as a slow, purging stream of argon was passed through the reaction vessel and into an acidified solution of 2,4-dinitrophenylhydrazine in ethanol. When gas evolution had ceased, 58 mg of acetaldehyde 2,4-dinitrophenylhydrazone (25%) was isolated, mp 161–163 °C (lit. 148, 168 °C) after recrystallization. It was identified by mixture melting point and ir spectral comparison.

***Reactions of the Epoxyethylsilanes with Amines.* A. Epoxyethyl(triphenyl)silane (2a).** A solution of 3.0 g (10 mmol) of **2a** in 30 ml of benzylamine (distilled beforehand from phosphorus pentoxide) was heated at 160–165 °C for 12 h. Removal of the amine by distillation at reduced pressure and trituration of the solid residue with benzene gave a colorless powder, mp 218–222 °C (92%), which was recrystallized from xylene, mp 228–229 °C. By mixture melting point and infrared spectral comparison this substance was shown to be hexaphenyldisiloxane (**12**).[4]

In a search for intermediates, 1:1 and 1:2 neat mixtures of **2a** and benzylamine were heated in an NMR tube at 150–155 °C for various periods and then examined by NMR spectroscopy ($CDCl_3$). After 15–30 min new peaks appeared at 0.8 (d, J = 5 Hz), 1.05 (d, J = 5 Hz), 1.60 (d, J = 5 Hz, ca. thrice as intense as the other doublets), and 4.15 ppm (br, s, ca. same intensity as peak at 1.60). These peaks persisted up to 1 h, but after 45 min hexaphenyldisiloxane (**12**) began to precipitate. Attempts to isolate acetaldehyde 2,4-dinitrophenylhydrazone by treating the final reaction mixture with acidified, ethanolic 2,4-dinitrophenylhydrazine gave only solids melting over a broad range.

Similarly, heating a 1:1 mixture of **2a** and anhydrous morpholine at 150–155 °C for 15 min caused the appearance of new doublets in the NMR spectrum: 0.95 (J = 6 Hz) and 1.12 ppm (J = 6.5 Hz) in an intensity ratio of 2:1.

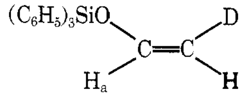
When a solution of **2a** (1.5 g, 5 mmol) and anhydrous piperidine (1 ml, 5 mmol) in 25 ml of xylene was heated at reflux for 10 h and the solvent then removed, dilution of the residue with ether gave 0.3 g of hexaphenyldisiloxane (**12**, 23%). Chromatography of the mother liquor on Florisil and elution with ether gave 0.9 g of impure triphenylsilanol (**4a**, 66%, mp 126–145 °C). This solid melted at 152–155 °C after recrystallization from cyclohexane.

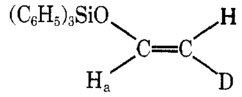
B. *cis*-β-Trimethylsilylstyrene Oxide (5a). Heating 1:1 mixtures of **5a** and anhydrous benzylamine at 150–155 °C and monitoring periodically by NMR analysis revealed new peaks after 20 min: 0.4 (s), 0.45 (s), 0.48 (s), 2.12 (d, J = 5 Hz), 3.15 (br s), and 4.47 ppm (d, J = 5 Hz). The peaks at 2.12, 3.15, and 4.47 ppm were of the same intensity. After 60 min the epoxide peaks had almost disappeared and the singlet at 0.48 ppm had increased relative to that at 0.5 ppm.

A similarly conducted reaction between **5a** and anhydrous morpholine revealed after 45 min at 150–155 °C that new peaks developed at 0.40 (s), 0.45 (s), 0.64 (s), 3.33 (d, J = 5 Hz), and 4.32 ppm (d, J = 5 Hz).

Pyrolysis of Epoxyethyl(triphenyl)silanes. A. Undeuterated Silane (2a). A 200-mg sample of epoxyethyl(triphenyl)silane was heated in an NMR tube under a dry nitrogen atmosphere for 2 h at an oil bath temperature of 290 ± 10 °C. Cooling of the sample, dissolution in deuteriochloroform, and recording of the NMR spectrum showed that 40% of **2a** had isomerized to triphenyl(vinyloxy)silane (**13**).

B. α-Deuterioepoxyethyl(triphenyl)silane (2c). When this compound was heated at 275 ± 5 °C for 1.5 h, a 25% conversion to the corresponding triphenyl(vinyloxy)silane was realized. Doublets in relative intensities of 3:1 were observed at 4.05 and 4.53 ppm, which corresponded to the presence of i (J = 6 Hz) and ii (J = 14 Hz), respectively; a complicated multiplet ascribable to the H_a proton was centered at 6.35 ppm. In other runs, narrow multiplets were observable within the individual doublets centered at both 4.05 and 4.53 ppm. These multiplets indicate the probable presence of some $(C_6H_5)_3SiOCD{=}CH_2$. The ratio of such α-deuteriovinyloxy product to the total of the β-deuteriovinyloxy products was ca. 20:80.


i


ii

C. α-Deuterioepoxyethyl(triphenyl)silane (2c) under Varying Conditions. There was some indication that thermal rearrangements occurred more readily when conducted in NMR tubes that had been soaked in chromic acid solution and just rinsed in distilled water. Accordingly, the following runs were conducted in NMR tubes which were cleaned in chromic acid solution, soaked in aqueous sodium bicarbonate solution, and repeatedly rinsed with distilled water.

Three comparative pyrolyses were carried out in NMR tubes on 100–200 mg of **2c** for 2 h at 270 ± 5 °C. Upon cooling an accurately known quantity of toluene was added (30–40 mg) as an internal standard, the sample diluted with a known quantity of deuteriochloroform, and the NMR spectrum recorded. The conditions of pyrolysis, percentage of **2c** remaining, percentage of vinyloxysilane, and ratio of β-*cis*:β-*trans* $(C_6H_5)_3SiO(D)C{=}CH_2$ pertinent to each run were the following: (1) under a nitrogen atmosphere, 55% of **2c**, 45% of **13** in a 66:33 ratio; (2) with 0.5% by weight of hydroquinone, 80% of **2c**, 20% of **13** in a 75:25 ratio; and (3) in air, 80% of **2c**, 20% of **13** in a 75:25 ratio (error limits of ±10%).

Rearrangement of α-Deuterioepoxyethyl(triphenyl)silane (2c) to β-Triphenylsilylacetaldehyde (10) by Means of Magnesium Bromide Etherate. Magnesium bromide etherate was prepared by adding ethylene bromide to a stirred suspension of an equivalent amount of magnesium turnings in dry diethyl ether. Then a solution of 1.20 g (4 mmol) of **2c** in 20 ml of benzene was treated with an excess of magnesium bromide etherate and the solution refluxed for 1 h. Workup according to a published procedure gave the aldehyde (**10**), whose NMR spectrum showed the characteristic doublet at 2.97 ppm in addition to a broadened singlet within this doublet. At 9.61 ppm a clear doublet was evident (4 Hz). These signals are consistent with the presence of both $(C_6H_5)_3SiCHDCHO$ (**10a**) and $(C_6H_5)_3SiCH_2CDO$ (**10b**) in ca. equal amounts.

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Registry No.—**1a,** 18666-68-7; **1b,** 59231-24-2; **1c,** 59231-25-3; **2a,** 18666-55-2; **2b,** 59231-26-4; **2c,** 59231-27-5; **4a,** 791-31-1; **5a,** 56920-26-4; **5b,** 56920-25-3; **9,** 59231-28-6; **11,** 59231-29-7; (*E*)-trimethyl(β-styryl)silane, 19372-00-0; (*Z*)-trimethyl(β-styryl)silane, 19319-11-0; ethynyl(triphenyl)silane, 6229-00-1; diisobutylaluminum deuteride, 59231-30-0; α-deuteriovinyl chloride, 4984-12-7; phenyllithium, 591-51-5; tetraphenylsilane, 1048-08-4; diisobutylaluminum hydride, 1191-15-7; hydrogen chloride, 7647-01-0; chlorotriphenylsilane, 76-86-8; benzylamine, 100-46-9.

References and Notes

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(17) (a) P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, **97,** 1464 (1975). (b) The stereospecific syn elimination of trimethylsilanol, observed in the treatment of β-hydroxyalkylsilanes with potassium hydride in a tetrahydrofuran medium, may well ensue in a manner similar to that of pathway b in Scheme I, except that the carbanion resulting from the silicon–oxygen migration would have to be too short lived to undergo inversion. Alternatively, pathway a might be considered as offering a four-centered cyclic *intermediate* **19,** *whose collapse* would *yield* the olefin stereospecifically. However, orbital symmetry considerations would argue against a concerted passage from this planar intermediate to the olefin and the trialkylsilanoate anion, since this would be a thermally forbidden $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ process. Cf. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1971, p 172.

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Demethylations of Quaternary Pyridinium Salts by a Soft Nucleophile, Triphenylphosphine. Electronic and Steric Accelerations[1]

Ulf Berg,[2] Roger Gallo, and Jacques Metzger*

I.P.S.O.I., Faculté des Sciences de St Jérôme, rue Henri Poincare, 13013 Marseille, France

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N-Methyl quaternary pyridinium salts are easily demethylated by PPh_3 in DMF. The relative rate constants are determined by NMR with a competition technique for 18 compounds. The range of reactivity is 10^3. The reaction is accelerated with electron-withdrawing substituents on the pyridine ring. The Hammett and Brønsted equation constants are $\rho = +2.34$; $\alpha = +0.387$. Ortho substituents increase the rate constants by strain release (a factor of 103 for the 2-*t*-Bu). The correlation with the opposite quaternization reactions is excellent (correlation coefficient $R = 0.994$). Linear free-energy relationships are obtained both with electronic and steric parameters, and give further insight into the structure of the transition state of these reactions.

Compared to the number of mechanistic and structural studies on the quaternization of pyridines,[3] no quantitative results have yet been reported for dequaternization of pyridinium salts.

Until recently no general method existed for N-dealkylation of quaternary salts of heteroaromatic amines. The techniques applied to ammonium salts are inadequate: they use hard nucleophiles and (or) high temperatures,[4–15] so that sensitive