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1,*n*-TRIORGANOSILYL MIGRATIONS IN THE REARRANGEMENTS OF SILYL-SUBSTITUTED ORGANOLITHIUM COMPOUNDS *

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Summary

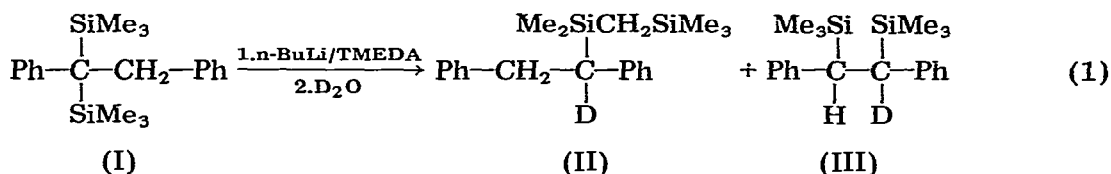
Under the agency of the potent lithiating agent, *n*-butyllithium in TMEDA, an array of organosilanes was found to undergo 1,*n*-silyl rearrangements via carbanionic intermediates. Unambiguous 1,2-, 1,3- and 1,4-silyl shifts were uncovered in 1-trimethylsilyl-1,1,2-triphenylethane, 1,1-bis(trimethylsilyl)-1-phenylalkanes and 1,2-bis(trimethylsilyl)-1,2-diphenylethane, respectively. Cross-over and competition experiments established that these rearrangements generally are intramolecular and occur with decreasing ease in the order, 1,2 > 1,3 ≧ 1,4. In other compounds, such as 1,1-bis(trimethylsilyl)-1,2-diphenylethane, 1,*n*-bis(trimethylsilyl)benzenes and triphenyl(trimethylsilyl)methane, competing 1,*n*-silyl shifts occurred. Attack of the organolithium intermediates on solvent and silicon–lithium exchange were significant side reactions in some instances. 1-Trimethylgermyl-1,1,2-triphenylgermane underwent no discernible rearrangement but rather gave the product expected from germanium–lithium exchange. By conducting time and competition studies, it was shown that lithiation is the product-determining step in these rearrangements and that dual pathways, namely 1,3- versus consecutive 1,2- and 1,4-pathways, are operative in certain rearrangements.

* Part 15 of the series, "Organosilicon Compounds with Functional Groups Proximate to Silicon" (previous part: *J. Amer. Chem. Soc.*, 98 (1976) 4646), as well as Part 18 of the series, "Rearrangements of Organometallic Compounds" (previous part: *J. Organometal. Chem.*, 160 (1978) C8.).

** Dedicated to Professor Henry Gilman, from whom this former student was privileged to acquire the training and the zeal for organometallic chemical research. The intertwining themes of the present article, namely organolithium and organosilicon chemistry, are particularly apt for this dedicatory Issue, since Professor Gilman has been a pre-eminent leader in these areas for over 50 years.

Introduction

In a study seminal for the discovery of anionic organosilicon rearrangements, Gilman and Wu reported in 1953 that triphenylsilylpotassium reacts with benzophenones to yield, after hydrolysis, diaryl-methoxy(triphenyl)silanes [1]. Their suggestion that this product could have arisen by rearrangement of the initially formed potassium diaryl(triphenylsilyl)methoxide was borne out by the masterly research of Brook [2]. During the last 25 years intramolecular rearrangements of triorganosilyl groups induced by anionic oxygen, nitrogen or sulfur centers have been the subject of extensive studies, principally by West [3,4] and by Brook [5,6]. The occurrence of corresponding migrations of triorganosilyl groups between carbanionic sites, however, was first recognized in 1973, when 1,1-bis-(trimethylsilyl)-1,2-diphenylethane (I) was treated with *n*-butyllithium in TMEDA [7] (eq. 1):

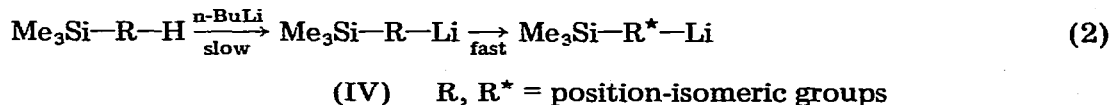


The formation of II and III in a final ratio of 18 : 1 could have ensued as a consequence of 1,2-, 1,3- and/or 1,4-silyl shifts between anionic sites. Accordingly, the following studies on a wide variety of organosilicon compounds were carried out, in order to determine the scope and the paths of such anionic rearrangements.

Results

Carbanionic nature of the rearrangements

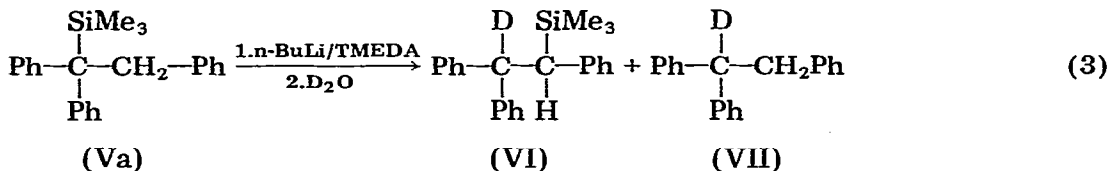
That organolithium compounds are the reactive intermediates in these rearrangements can be concluded from two observations: 1) the reaction requires the presence of *n*-butyllithium with strong Lewis bases, such as *N,N,N',N'*-tetramethylethylenediamine or tetrahydrofuran; and 2) treatment of reaction mixtures with D_2O yields rearrangement products labeled with deuterium (eq. 1). From time- and temperature-dependence studies it can further be concluded that the lithiation step of the organosilane is much slower than the silyl migration step, for deuterium incorporation in the recovered starting material has not been observed (eq. 2):



For example, when the reaction in eq. 1 was conducted at -25°C , and aliquots taken during the first half of the conversion were worked up with D_2O , recovered I was found to be free of deuterium and II and III were proved to be essentially monodeuterated as shown. Thus, IV does not persist in the reaction mixture.

Unambiguous 1,*n*-silyl shifts

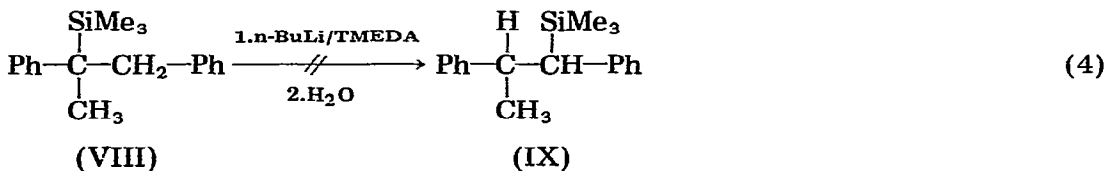
a) *1,2-Shift*. The treatment of 1-trimethylsilyl-1,1,2-triphenylethane (Va) with *n*-butyllithium in TMEDA at 25°C for 6 days gave a 60% conversion to a 5 : 1 mixture of 2-trimethylsilyl-1,1,2-triphenylethane (VI) and 1,1,2-triphenylethane (VII) (eq. 3):



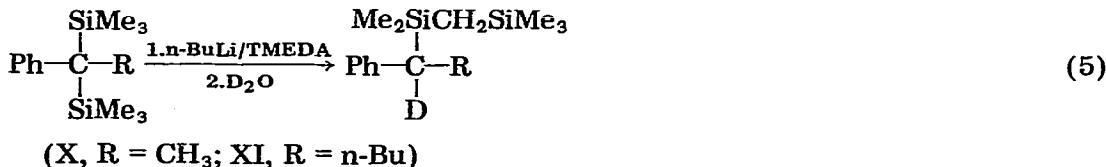
Under similar conditions, 1-ethyldimethylsilyl-1,1,2-triphenylethane (Vb) rearranged to yield its 2-ethyldimethylsilyl isomer and VII in a 10 : 1 ratio with a 20% conversion.

The hydrocarbon VII apparently arose by direct displacement of the silyl group in V by *n*-butyllithium. With the corresponding germanium compound, 1-trimethylgermyl-1,1,2-triphenylethane, treatment with *n*-butyllithium in TMEDA yielded no discernible 1,2-germyl shift, as in VI, but only the displacement product VII could be identified in the reaction mixture.

The reaction of eq. 3 is essentially irreversible, for treatment of VI with base resulted in no change. The importance of greater anionic stability in promoting a rearrangement was further reflected in the failure of VIII to yield IX (eq. 4):



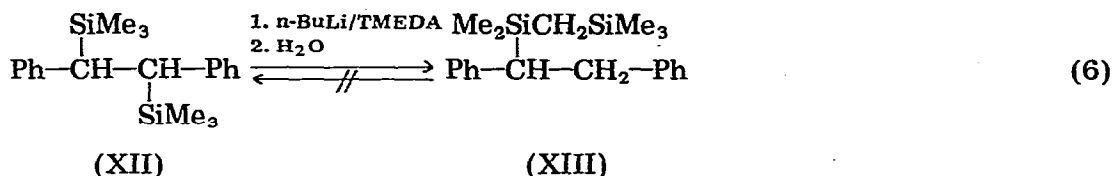
b) *1,3-Shift*. Under the foregoing conditions, both 1,1-bis(trimethylsilyl)-1-phenylethane (X) and the corresponding 1-phenylpentane (XI) derivatives underwent 1,3-silyl migrations to about a 65% conversion (eq. 5):



In the absence of any available benzylic proton, lithiation and hence rearrangement occur on the methyl groups.

c) *1,4-Shift*. Under comparable conditions, 1,2-bis(trimethylsilyl)-1,2-diphenylethane (XII) was markedly less reactive than its 1,1-bis(trimethylsilyl) isomer (I) and rearranged in about 20% conversion to yield 1-[dimethyl(trimethylsilylmethyl)silyl]-1,2-diphenylethane (XIII). The structure of this product could be assigned on the basis of its ¹H-NMR spectrum and upon its cleavage

with alcoholic potassium hydroxide to yield bibenzyl (eq. 6):



Again, the rearrangement is irreversible, for XIII was recovered unchanged after treatment with n-butyllithium.

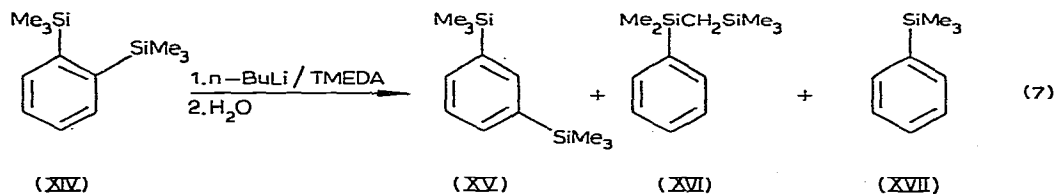
Cross-over and competition experiments

To test for the intramolecularity of these rearrangements, an equimolar mixture of 1,1-bis(trimethylsilyl)-1-phenylethane (X) and 1-ethyldimethylsilyl-1,1,2-triphenylethane (Vb) was treated with n-butyllithium and TMEDA. After 6 days at 25°C hydrolysis and GLC analysis revealed the presence of only the 1,3-rearrangement product of X (eq. 5) and the 1,2-shift product from Vb (eq. 3) in conversions of 83% and 31%, respectively. No cross-over products, such as 2-trimethylsilyl-1,1,2-triphenylethane (VI) and 1-[dimethyl(ethyldimethylsilyl-methyl)silyl]-1-phenylethane, were detected. Although the extent of the 1,3-shift in X was more than 2.5 times the amount of the 1,2-shift in Vb, it should be noted that the ratio of replaceable protons in X and Vb is 9 : 1. If the CH_3Si protons in X and the CH_2Ph protons in Vb were to have comparable kinetic acidities, then the results would mean the 1,2-shift in Vb was actually somewhat faster than the 1,3-shift in X.

Likewise, in a competition experiment an equimolar mixture of 1-trimethylsilyl-1,1,2-triphenylethane (Va) and 1,2-bis(trimethylsilyl)-1,2-diphenylethane (XIII) underwent rearrangement with n-butyllithium to produce VI and XIII in a ratio of 1.2 : 1.0. Since the ratio of the pertinent protons here (CH_2Ph vs. CH_3Si) is 1 : 9, the 1,2-shift in Va occurs considerably more readily than the 1,4-shift in XIII.

Competing 1,n-silyl shifts

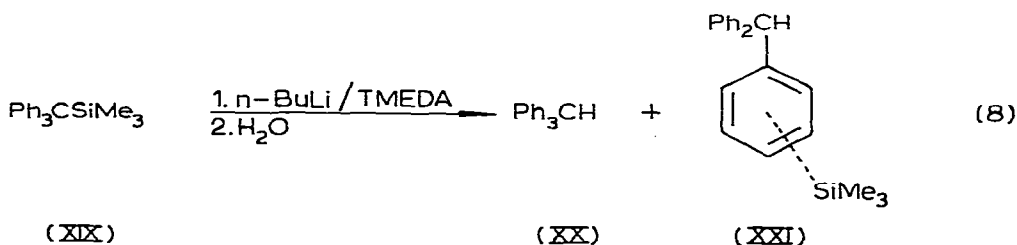
When the *ortho*-, *meta*- and *para*-bis(trimethylsilyl)benzenes were individually treated with n-butyllithium and TMEDA, only the *ortho* isomer (XIV) underwent rearrangement (eq. 7):



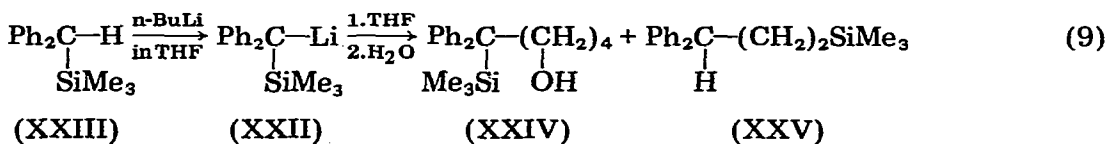
The 1,2- and 1,4-rearrangement products, XV and XVI, were formed in a 1.2 : 1.0 ratio. Since the available metallation sites of XIV statistically favor a 1,4-shift in a ratio of 9 : 1 (CH_3Si versus C_3H and C_6H), here again the 1,2-shift actually occurs more rapidly. The formation of trimethylsilylbenzene (XVII) was minor with the *ortho* isomer (3% of the products). When *para*-bis(trimethyl-

silyl)benzene (XVIII) was treated with base, only displacement of the trimethylsilyl occurred to form XVII in 10% yield. The *meta* isomer (XV), however, formed 60% of XVII under the same reaction conditions.

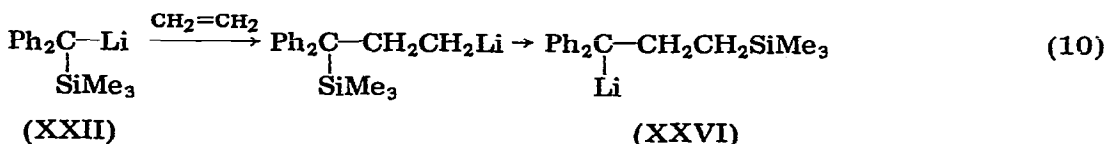
Similar competing rearrangements were observed when triphenyl(trimethylsilyl)methane (XIX) was exposed to an excess of *n*-butyllithium. Upon hydrolysis, the major product was triphenylmethane (XX, 81%), presumably resulting by direct displacement of the trityl anion by *n*-butyllithium. The remaining 19% of the product was a mixture of the *ortho*, *meta* and *para* isomers of XXI in a 1.1 : 3.8 : 1.0 ratio (eq. 8):



An unusual variant of these rearrangements is that encountered with diphenyl(trimethylsilyl)methylithium (XXII) in tetrahydrofuran solution. Generation of XXII from XXIII with *n*-butyllithium in THF produces, upon hydrolysis, a 1 : 1 mixture of 5,5-diphenyl-5-trimethylsilylpentanol (XXIV) and 3-trimethylsilyl-1,1-diphenylpropane (XXV) (eq. 9):



It appears that both XXIV and XXV stem from the THF: a) XXIV could be the simple cleavage product of THF by XXII, a reaction for which there is precedent in the chemistry of Ph_3SiM reagents [8]; and b) XXII could undergo ethylene insertion (which results from the attack of *n*-butyllithium on THF itself [9,10]) and the adduct then undergo a 1,3-silyl shift to yield XXVI (eq. 10):

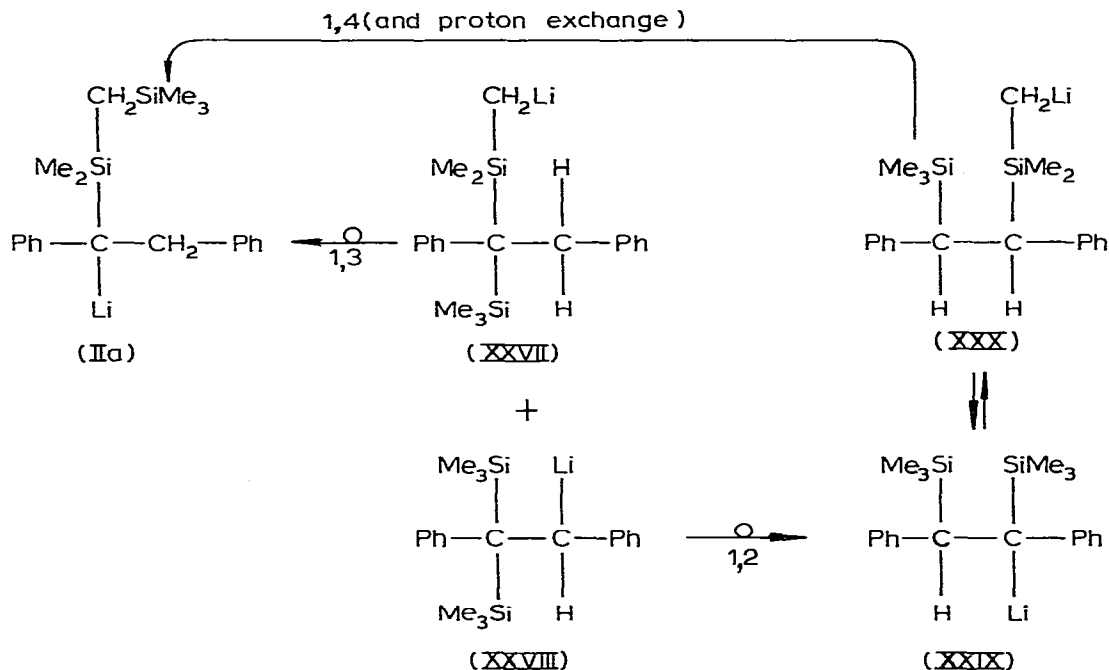


Competing 1,*n*-silyl shifts with 1,1-bis(trimethylsilyl)1,2-diphenylethane (I)

Since these results demonstrate the possibility of 1,2-, 1,3- and 1,4-silyl shifts, the products formed from 1,1-bis(trimethylsilyl)-1,2-diphenylethane could have arisen via two competing pathways (eq. 1). Structure IIa could have been formed directly from I via a 1,3-silyl shift of anion XXVII; or it could have arisen by a 1,2-silyl shift of anion XXVIII to produce XXIX, which may equilibrate with XXX. Compound XXX could then form IIa by 1,4-silyl shift (Scheme 1).

Insight into the relative importance of these alternative pathways for eq. 1 was gained by performing a time study on the ratio of II to III as the reaction time

SCHEME 1



at 25°C was varied from 10 minutes to 96 h. Initially, after 10 minutes the ratio of II to III was 6.6; after 96 h it was 15.0 and the reaction was 95% complete. If the ratio of these rearrangement products were determined simply by the rates of formation of anions XXVII and XXVIII (the respective 1,3- and 1,2-shifts leading to II and III being relatively faster), this ratio should be invariant with time. Such constancy in the product ratio constitutes, in fact, the Wegscheider test for simultaneous side reactions proceeding from the same reactant and having the same reaction order [11]. The change in the ratio of II to III with time implies that II is also being formed by a separate pathway. Since III is known to rearrange slowly to yield II, this additional source of II here must be a consecutive 1,2- and 1,4-silyl migration pathway. Further, some estimate of the relative importance of the 1,3-path over the consecutive 1,2- and 1,4-path can be made. Early in the reaction when the ratio of II and III is essentially determined by the relative rates at which anions XXVII and XXVIII are formed (there being little contribution from any 1,2- + 1,4-shifts), the ratio of 6.6 : 1.0 can be taken as an approximate ratio of rate constants for the formation of II and III (eq. 11).

$$\frac{d(\text{XXVII})}{d(\text{XXVIII})} = \frac{k_1[\text{I}][\text{RLi}]^x}{k_2[\text{I}][\text{RLi}]^x} = \frac{[\text{XXVII}]}{[\text{XXVIII}]} = \frac{k_1}{k_2} \quad (11)$$

A ratio of 6.6 : 1.0 for k_1/k_2 means that early in the reaction $(6.6/7.6) \times 100$ or 86% proceeds to yield II directly. Accordingly, a minimum of 14% of the

reaction produces III and, eventually, II via a consecutive 1,2- and 1,4-silyl shift.

Discussion

The foregoing results establish that 1,*n*-silyl shifts in silyl-substituted organolithium compounds tend to occur intramolecularly and to produce resonance-stabilized organolithium compounds. Even though benzylic lithium intermediates may be generated in the course of these rearrangements, those final products will be favored that have a carbon-lithium *alpha* to two or more phenyl or silyl groups (e.g., II, III, and VI). In some instances, as for example in the rearrangement of triphenyl(trimethylsilyl)methane (XIX), it is difficult to conceive an intramolecular path leading to the trimethylsilyl-substituted triphenylmethanes (XXI in eq. 8). An intermolecular path involving trityllithium and XIX may be operative here.

As to the relative ease of 1,2-, 1,3- and 1,4-silyl shifts, quantitative ranking is not yet possible. However, if one considers the extent of rearrangement under comparable reaction conditions and makes statistical adjustments for the nature of replaceable hydrogens in the silyl substrates being compared, a qualitative ordering of 1,*n*-silyl migrations can be made. In 1,1-bis(trimethylsilyl)-1,2-diphenylethane (I) the ratio of rate constants for metalating the Me₃Si group (*k*₁) and the CH₂Ph group (*k*₂) has been estimated at 6.6 : 1.0. If one takes into account the statistical representation of protons, one obtains (eq. 12):

$$\frac{k_1 \times 9}{k_2 \times 1} = \frac{6.6}{1.0} \quad \text{or} \quad k_1 = 0.7k_2 \quad (12)$$

This suggests that the lithiation leading to the 1,2-shift is somewhat faster than that required for the 1,3-silyl shift. Furthermore, the competitive rearrangements of 1-trimethylsilyl-1,1,2-triphenylethane (Va) and 1,2-bis(trimethylsilyl)-1,2-diphenylethane (XIII) support the conclusion that *k*₃(Va) \simeq *k*₄(XIII). With statistical correction for replaceable protons, the rate constant ratio becomes (eq. 13):

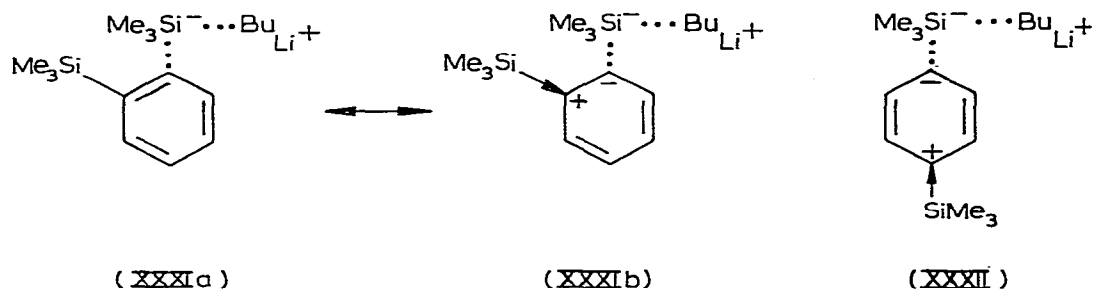
$$\frac{k_3 \times 1}{k_4 \times 9} = \frac{1.2}{1.0} \quad \text{or} \quad k_3 = 11k_4 \quad (13)$$

Again, in accord with other findings, the lithiation required for the 1,2-shift is considerably faster than that needed for the 1,4-shift. The resulting ranking of these silyl shifts as 1,2 > 1,3 \gg 1,4 may simply reflect the greater kinetic acidity of the CH₂Ph group over that of the CH₃Si function.

There is independent evidence that benzylic protons are more readily replaced than methylsilyl protons. The complex of *n*-butyllithium with TMEDA can metalate toluene at 25°C to a 90% conversion [12,13] within 0.5 h. Tetramethylsilane yields only 36% of trimethylsilylmethylolithium from the same reagent after 3 days.

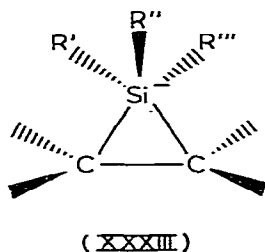
With some of the substrates examined, silicon-lithium exchange was strongly competitive with hydrogen-lithium exchange and the ensuing rearrangement. Especially where highly stabilized lithium compounds would result were such

silicon—lithium exchanges prominent, as with Va leading to 1,1,2-triphenyl-ethylolithium and with XIX yielding a trityllithium. Noteworthy is the observation that, of the three bis(trimethylsilyl)benzenes, the *meta* isomer was most prone to undergo such an exchange (60% versus 3% and 10% for the *ortho* and *para* isomers). The build-up of negative charge in the transition state of such exchanges may be retarded by the electron release of an *ortho* (XXXI) or *para* (XXXII) Me₃Si group. No such destabilization would be encountered in the transition state for *meta* exchange.



Also, the attempted rearrangement of 1-trimethylgermyl-1,1,2-triphenylethane gave no discernible rearrangement but only germanium—lithium exchange to yield 1,1,2-triphenylethyllithium. The greater electronegativity of germanium may facilitate nucleophilic attack by the butyl anion on the germanium center.

As has been found in other anionic silyl rearrangements [3,4], migrations of organic groups such as phenyl in I are not at all competitive with the extremely rapid silyl migrations. The intramolecularity of many of these silyl migrations strongly suggests that the silyl group migrates through a pentacoordinate silicon intermediate (XXXIII), and thus retains its configuration. However, such assumptions will require experimental proof.



Finally, these novel 1,*n*-silyl shifts between carbanionic centers open up fresh approaches for studying nucleophilic substitution mechanisms in organosilanes, as well as for preparing unusual silicon—carbon skeletons.

Experimental

General techniques used for handling moisture- and oxygen-sensitive reagents

All the processes for the preparation, storage and transformation of organometallic substances and their solvents were conducted in an atmosphere of dry and oxygen-free nitrogen. For further purification of nitrogen gas (Air Products, Ultra High Purity, 99.9%) from oxygen and water vapor, nitrogen gas was

passed through a column (80 × 2.5 cm) of reduced copper (B.T.S. Katalysator, Badische Anilin und Soda-Fabrik A.G., Ludwigshafen am Rhein), and then through a column (80 × 2.5 cm) of anhydrous calcium sulfate (Drierite, 8 mesh) and phosphorus pentoxide granules (J.T. Baker Co.) supported on glass beads.

All glassware to be in contact with organometallic reagents was dried at 150°C for at least five hours and flushed with dry, oxygen-free nitrogen. The hypodermic syringes were dried under vacuum and flushed with dry nitrogen.

Tetrahydrofuran (THF, Fisher) was dried under an inert atmosphere of dry nitrogen by refluxing over pieces of sodium metal for at least twelve hours. Distillation of the solvent into a flask containing lithium aluminum hydride and then refluxing over lithium aluminum hydride for at least four hours before use completed the purification. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, Aldrich) was dried by refluxing over calcium hydride powder for at least twelve hours under an atmosphere of dry nitrogen. All hydrocarbon solvents were dried by heating at reflux over sodium metal with a trace of benzophenone, until the color of ketyl radical-anion persisted. All solvents were freshly distilled from the drying agent into a dry nitrogen-purged reaction vessel just prior to reaction. Anhydrous diethyl ether was purchased in sealed cans (Fisher), which were opened just before use.

Melting points were determined in capillary tubes with a Thomas-Hoover "Uni-melt" apparatus and are uncorrected. The nuclear magnetic resonance spectra were measured with a Varian spectrometer, Model A-60. Signals are reported using the δ scale in parts per million from trimethylsilyl groups or tetramethylsilane as an internal standard for chemical shifts, followed by the integrated intensities of the proton signals, and the coupling constants (*J*) in hertz. Infrared spectra were recorded on samples spread on sodium chloride disks, as mineral oil suspensions, or as solutions in pure solvents, by means of a Perkin-Elmer grating infrared spectrometer, Model 457. Mass spectra were recorded on a Perkin-Elmer mass spectrometer, Model 270, and a spectrum of perfluorokerosene was used to provide standard mass markings. The gas-liquid chromatographic analyses were performed on an F&M, dual-column program-temperature gas chromatograph, Model 720, equipped with a thermal conductivity detector. Elemental analyses were carried out by the Spang Micro-analytical Laboratory, Ann Arbor, Michigan.

Preparation of starting materials

1. *1,1-Bis(trimethylsilyl)-1,2-diphenylethane*. α,α -Bis(trimethylsilyl)toluene [14] was prepared by the metalation of benzyltrimethylsilane with *n*-butyllithium in tetrahydrofuran, followed by quenching with chlorotrimethylsilane and purification by vacuum distillation.

α,α -Bis(trimethylsilyl)toluene (6.4 g, 26 mmol) in 30 ml of dried tetramethylethylenediamine was treated dropwise with 12.2 ml (26 mmol, 2.1 *N* in *n*-hexane) of *n*-butyllithium. The resulting suspension was stirred at room temperature for 20 h and then treated with 3.2 g (26 mmol) of benzyl chloride. The color of the reaction mixture changed to light yellow. Thereupon the reaction mixture was hydrolyzed and extracted with ether. After ether extracts were dried with anhydrous magnesium sulfate, the volatile components were removed under reduced pressure. The residual product obtained was recrystal-

lized from ethanol to give 5.7 g (70%) of a colorless solid, m.p. 91–92°C. Spectral data: $^1\text{H NMR}$ (CDCl_3) δ 0.00(s, 18 H), 3.32 (s, 2 H), and 6.70–7.12 ppm (m, 10 H); IR (CCl_4) 3040w, 2980s, 1600m, 1400m, 1205s, 850s, 750s and 690s cm^{-1} ; MS (m/e , relative intensity, assignment) 326, 2.5, P ; 311, 5.7, $P - \text{CH}_3$; 253, 17.1, $P - \text{SiMe}$; 180, 2.8, $P - 2 \text{SiMe}_3$; 73, 100.0, SiMe_3 .

Anal. Found: C, 73.80; H, 9.30. Calcd. for $\text{C}_{20}\text{H}_{30}\text{Si}_2$: C, 73.62; H, 9.20%.

2. α -Bromo- α,α -bis(trimethylsilyl)toluene. A 500 ml, three-necked flask, equipped with a mechanical stirrer and a reflux condenser topped with an oxygen-free dry nitrogen inlet, was charged with a mixture of 20 g (84 mmol) of α,α -bis(trimethylsilyl)toluene, 16.4 g (92 mmol) of *N*-bromosuccinimide [15] and 5 g of anhydrous potassium carbonate in 250 ml of redistilled carbon tetrachloride. The mixture was heated at reflux while being stirred vigorously for 24 h. The orange mixture was cooled and filtered and the residue, which consisted chiefly of succinimide, was washed with carbon tetrachloride. The combined filtrate and washings were evaporated on the rotary evaporator to give a crude orange product. Fractional distillation of the crude product gave 18.6 g (70%) of the desired product, b.p. 84–85°C at 0.40 mmHg. Spectral data: $^1\text{H NMR}$ (neat) δ 0.00 (s, 18 H) and 7.30–6.70 ppm (m, 5 H); IR (neat) 3040w, 2970s, 1480s, 1260s, 850s, 755m and 690s cm^{-1} ; MS (m/e , assignment) 316, P ; 236; $\text{C}_6\text{H}_5 - \text{CH} - (\text{SiMe}_3)_2$; 162, $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{SiMe}_3$.

Anal. Found: C, 49.56; H, 7.32. Calcd. for $\text{C}_{13}\text{H}_{23}\text{Si}_2\text{Br}$: C, 49.49; H, 7.35%.

3. 1,1-Bis(trimethylsilyl)-1-phenylpentane. A 100-ml, two-necked flask, equipped with a magnetic stirring assembly, nitrogen inlet tube and serum cap, was charged with 5 g (15.8 mmol) of α,α -bis(trimethylsilyl)- α -bromotoluene in 50 ml of dried tetrahydrofuran. To this chilled (ice-water) mixture was added dropwise 6.6 ml (15.8 mmol, 2.2 *N* in *n*-hexane) of *n*-butyllithium via a syringe over a period of 10 min. After 4 h of stirring at room temperature, the reaction mixture was treated with water. The usual work-up procedure gave the crude product. The GLC analysis of the crude product showed the following product distribution: α,α -bis(trimethylsilyl)toluene (18%), 1,1-bis(trimethylsilyl)-1-phenylpentane (44%) and unchanged starting material (38%). Fractional distillation through a short column packed with glass helices gave the desired product, b.p. 94–95°C at 0.33 mmHg. Spectral data: $^1\text{H NMR}$ (neat) δ 0.00 (s, 18 H), 7.05–7.20 ppm (m, 5 H); IR (neat) 3040w, 2980s, 1380m, 1250s, 1170s, 850s, 705s, 680s, and 530s cm^{-1} ; MS (m/e , relative intensity assignment) 293, 1.85, $P + 1$; 292, 9.3, P ; 277, 1.8, $P - \text{CH}_3$; 218, 11.1, $P - \text{SiMe}_3$; 204, 48.1, $P - \text{SiMe}_4$; 145, 9.2, $P - 2 \text{SiMe}_3$; 100, SiMe_3 .

Anal. Found: C, 68.87; H, 10.71. Calcd. for $\text{C}_{17}\text{H}_{32}\text{Si}_2$: C, 68.83; H, 10.87%.

4. 1,1-Bis(trimethylsilyl)-1-phenylethane. To a flask equipped as described in section 3, 14.4 ml of methylithium (31.6 mmol, 2.2 *N* in diethyl ether) was introduced via a syringe into a chilled (ice-water bath) solution of 10 g (31.6 mmol) of α,α -bis(trimethylsilyl)- α -bromotoluene in 100 ml of dried tetrahydrofuran. The solution, which turned dark brown instantly upon addition of methylithium, was stirred at room temperature for 4 h and then hydrolyzed. Usual work-up and drying with anhydrous magnesium sulfate yielded a dark

brown crude product. The GLC analysis (6 ft column with 10% SE-30 on Chromosorb W and programmed to heat at a rate of 2°C/min between 150°C and 280°C) of the crude product indicated the main products distribution as α,α -bis(trimethylsilyl)toluene (18%), 1,1-bis(trimethylsilyl)-1-phenylethane (62%) and starting material (20%). Distillation provided the 1,1-bis(trimethylsilyl)-1-phenylethane, as a colorless liquid, b.p. 68–69°C at 0.40 mmHg. Spectral data: ¹H NMR (neat) δ 0.00 (s, 18 H), 1.32 (s, 3 H), and 7.01–7.20 ppm (m, 5 H); IR (neat) 3040s, 2980s, 1590s, 1470m, 1400m, 1250s, 850s, 750s, 680s, 620m, and 530s cm⁻¹; MS (*m/e*, relative intensity, assignment) 251, 3.1, *P* + 1; 250, 9.3, *P*; 235, 18.7, *P* – CH₃; 162, 75.0, *P* – SiMe₄; 147, 21.8, *P* – SiMe₃ – 2 CH₃; 104, 7.5, *P* – 2 SiMe₃; 73, 100, SiMe₃.

Anal. Found: C, 67.09; H, 10.50. Calcd. for C₁₄H₂₆Si₂: C, 67.11; H, 10.46%.

5. *Diphenylmethyl(trimethyl)silane*. This compound was prepared by a modification of the method of Hauser and Hance [16]. A suspension of diphenylmethylolithium in 100 ml of dried tetrahydrofuran was prepared from 8.4 g (49.9 mmol) of diphenylmethane and 25 ml (49.9 mmol, 2.0 *N* in *n*-hexane) of *n*-butyllithium. To the stirred red suspension was added 5.4 g (49.9 mmol) of chlorotrimethylsilane, the red color being discharged within one hour. After standing overnight the mixture was hydrolyzed and extracted with ether, the ether extracts dried over anhydrous magnesium sulfate and the filtered extracts freed of solvent. The residual solid was recrystallized from diethyl ether to give 10.5 g (90%) of colorless crystals, m.p. 74–75°C [lit. 74.5–75.5°C], ¹H NMR spectrum (CDCl₃) δ 0 (s, 9 H), 3.52 (s, 1 H), and 7.13–7.14 ppm (m, 10 H).

6. *Triphenylmethyl(trimethyl)silane*. This compound was also prepared by a modification of the method described by Hauser and Hance [16]. Triphenylmethane (24 g, 100 mmol) was metalated by 45.4 ml (100 mmol, 2.2 *N* in *n*-hexane) of *n*-butyllithium over a 4 h period at room temperature. The red color of the trityllithium suspension was discharged on the addition of 10.8 g (100 mmol) of chlorotrimethylsilane. After standing overnight, the usual work-up procedure gave a light yellow solid. Recrystallization from diethyl ether gave 24 g (76%) of a white powder, m.p. 170–171°C [lit. 169.5–170.5], ¹H NMR spectrum (CDCl₃): δ 0 (s, 9 H), and 6.80–7.30 ppm (m, 15 H).

7. *1-Trimethylsilyl-1,1,2-triphenylethane*. A stirred solution of 24 g (100 mmol) of diphenyltrimethylsilylmethane in 200 ml of dried tetrahydrofuran was treated with 50 ml (100 mmol, 2.0 *N* in *n*-hexane) of *n*-butyllithium, which was added from a pressure-equalizing addition funnel. The resulting red solution was stirred at room temperature overnight and then 12.6 g (100 mmol) of benzyl chloride was added. The color of the mixture was discharged upon the addition of benzyl chloride. The reaction mixture was stirred at room temperature overnight and then hydrolyzed. Usual work-up, drying with anhydrous magnesium sulfate and solvent removal yielded a white solid. This solid was recrystallized from diethyl ether to give 18.1 g (80%) of white crystals, m.p. 94–95°C. Spectral data: ¹H NMR (CDCl₃) δ 0.00 (s, 9 H), 3.65 (s, 2 H) and 6.62–7.50 ppm (m, 15 H); IR (CCl₄): 3040w, 2980s, 1940w, 1870w, 1600s, 1500s, 1300s, 1080s, 1040s, 940m, 850s and 700s cm⁻¹; MS (*m/e*, assignment):

330, *P*; 256, Ph₂C=CHPh; 180, PhCH=CHPh; 73, SiMe₃.

Anal. Found: C, 83.64; H, 8.02. Calcd. for C₂₃H₂₆Si: C, 83.57; H, 7.92%.

8. *2-Trimethylsilyl-1,1,2-triphenylethane*. A 250 ml three-necked flask (with a two-way stopcock at the bottom), equipped with a mechanical stirrer and a pressure-equalizing additional funnel, was charged with 16.8 g (100 mmol) of diphenylmethane in 150 ml of dried tetrahydrofuran. To this mixture was added 45.5 ml (100 mmol, 2.2 *N* in *n*-hexane) of *n*-butyllithium, which caused the immediate development of a red solution. After stirring at room temperature for 12 h, this red suspension was drained through the bottom outlet into 24.1 g (100 mmol) of α -bromo- α -trimethylsilyltoluene dissolved in 50 ml dried THF, contained in a two-necked flask. The color of the solution of the anion was discharged immediately. Hydrolysis and work-up were carried out after stirring for 12 h at room temperature. The ether solution was concentrated under reduced pressure to give a brown oil. Fractional crystallization from chloroform gave 6.6 g (40%) of 1,1,2,2-tetraphenylethane. Further crystallization from petroleum ether (b.p. 38.2–47.6°C) gave 3.3 g (35%) of 1,2-bis(trimethylsilyl)-1,2-diphenylethane and crystallization over again from *n*-hexane gave 6.6 g (20%) of 2-trimethyl-1,1,2-triphenylethane, m.p. 141–142°C. Spectral data: ¹H NMR (CDCl₃) δ 0.00 (s, 9 H), 3.53 (d, 1 H, *J* = 13 Hz), 4.90 (d, 1 H, *J* = 13 Hz), and 7.28–7.88 ppm (m, 15 H); IR (CCl₄): 3040w, 2970w, 1930w, 1870w, 1790w, 1600s, 1490s, 1450s, 1250s, 1070m, 1030m, 850s and 700s cm⁻¹; MS (*m/e*, assignment); 331, *P* + 1; 330, *P*; 256, Ph₂C=CHPh; 167, Ph₂CH; 73, SiMe₃.

Anal. Found: C, 83.65; H, 7.84. Calcd. for C₂₃H₂₆Si: C, 83.57; H, 7.92%.

9. *Ethyldimethylsilyl(diphenyl)methane*. Chloro(ethyl)dimethylsilane was prepared in the standard manner by the reaction of dimethyldichlorosilane with ethylmagnesium bromide [17]. The red-colored suspension of diphenylmethyllithium in 200 ml dried tetrahydrofuran was obtained from the metalation of 16.8 g (100 mmol) of diphenylmethane in 150 ml of anhydrous tetrahydrofuran with 100 mmol of *n*-butyllithium (cf. section 8). To this red suspension, 12.3 g (100 mmol) of ethyldimethylchlorosilane was added. This mixture stood overnight at room temperature and then was worked up in the usual manner to give a yellow liquid. Fractional distillation gave 23.3 g (91.8%) of colorless liquid, b.p. 144–145°C at 0.4 mmHg. Spectral data: ¹H NMR (neat) δ 0.00 (s, 6 H), 0.33–0.99 (m, 5 H), 3.55 (s, 1 H), and 6.87–7.40 ppm (m, 10 H); IR (neat): 3040s, 2980s, 1600s, 1450m, 1390m, 1250s, 1075m, 850s, 750s and 700s cm⁻¹; MS (*m/e*, relative intensity, assignment): 255, 4.0, *P* + 1; 254, 19.6, *P*; 239, 1.5, *P* – CH₃; 225, 1.4, *P* – C₂H₅; 167, 7.3, *P* – EtSiMe₂; 87, 100.0, EtSiMe₂; 59, 97.5 SiMe₂.

Anal. Found: C, 80.09; H, 8.77. Calcd. for C₁₇H₂₂Si: C, 80.23, H, 8.72%.

10. *1-Ethyldimethylsilyl-1,1,2-triphenylethane*. The lithium derivative of ethyldimethylsilyl(diphenyl)methane was made by treating 19.08 g (750 mmol) of the compound in 100 ml of dried tetrahydrofuran with 31.2 ml (750 mmol, 2.4 *N* in *n*-hexane) of *n*-butyllithium in the cold (ice-water bath) over a one hour period. After the addition was completed, the reaction mixture was stirred

at room temperature for 12 h. To this red suspension 9.4 g (750 mmol) of benzyl chloride was added dropwise and the resulting suspension stirred at room temperature for 12 h. Usual work-up gave the crude product. Distillation provided 20.6 g (80%) of a viscous oil, b.p. 178–180°C at 0.4 mmHg. Spectral data: $^1\text{H NMR}$ (CDCl_3); δ 0.00 (s, 6 H), 0.40–1.20 (m, 5 H), 3.62 (s, 2 H), 6.60–7.48 (m, 15 H); IR (neat): 3040s, 2980s, 1600s, 1490s, 1450m, 1250s, 820s, 770s and 700s cm^{-1} ; MS (m/e , relative intensity, assignment), 345, 1.0, $P + 1$; 315, 1.0, $P - \text{C}_2\text{H}_5$; 256, 60.4, $P - \text{EtSiMe}_2$; 253, 1.1, $P - \text{C}_6\text{H}_5\text{CH}_2$; 180, 14.9, $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$; 178, 24.5, $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$; 87, 100.0, EtSiMe_2 ; 59, 99.9, SiMe_2 .

Anal. Found: C, 83.72; H, 8.24. Calcd. for $\text{C}_{24}\text{H}_{28}\text{Si}$: C, 83.65; H, 8.19%.

11. *2-Trimethylsilyl-1,2-diphenylpropane*. 1-Phenyl-1-trimethylsilylethane was prepared according to a published procedure [18]. Five grams (24 mmol) of 1-phenyl-1-trimethylsilylethane in 20 ml of dried N,N,N',N' -tetramethylethylenediamine were metalated by 10.6 ml (24 mmol, 2.25 N in n -hexane) of n -butyllithium. The red suspension was stirred overnight at room temperature, and then quenched with 3.03 g (24 mmol) of benzyl chloride. After stirring for 6 h, hydrolysis, extraction with ether, washing the extract with 10% aqueous hydrochloric acid, drying with magnesium sulfate and evaporation of the solvent under reduced pressure gave 6.0 g of crude product. Distillation under vacuum gave a 20% recovery of starting material. The residue solidified at room temperature. Recrystallization from n -hexane (cooled in a solid CO_2 -acetone bath) gave 4.7 g (75%) of a white solid, m.p. 50–51°C. Spectral data: $^1\text{H NMR}$ (CDCl_3) δ 0.00 (s, 9 H), 1.22 (s, 3 H), 2.82 (d, 1 H, $J = 14$ Hz), 3.64 (d, 1 H, $J = 14$ Hz) and 6.74–7.42 ppm (m, 10 H); IR (Nujol): 3040w, 2980s, 1600m, 1450s, 1370m, 850s, 750m and 700s cm^{-1} ; MS (m/e , assignment): 269, $P + 1$; 268, P ; 253, $P - \text{CH}_3$; 195, $P - \text{SiMe}_3$; 180, $P - \text{SiMe}_4$; 91, $\text{C}_6\text{H}_5\text{CH}_2$; 73, SiMe_3 .

Anal. Found: C, 80.59; H, 8.82. Calcd. for $\text{C}_{18}\text{H}_{24}\text{Si}$: C, 80.59; H, 8.95%.

12. *Diphenylmethyl(trimethyl)germane*. This compound has been made by an approach different from that already reported [19]. By following the procedure described in section 5, 5.91 g (30 mmol) of bromotrimethylgermane was added to the red suspension of diphenylmethylithium in dried tetrahydrofuran. Usual work-up and recrystallization with ethanol gave 7.2 g of white crystals, m.p. 61–62°C [lit. 60°C].

13. *1-Trimethylgermyl-1,1,2-triphenylethane*. To the solution of 4.2 g (147 mmol) of diphenylmethyl(trimethyl)germane in 40 ml of dried tetrahydrofuran solution, 6.7 ml (14.7 mmol, 2.2 N n -hexane) of n -butyllithium was added via a syringe. The red suspension was stirred at room temperature for 12 h and the color was discharged upon addition of 1.61 g (14.7 mmol) of benzyl chloride. Hydrolysis and usual work-up yielded a crude oil. Upon standing the oil solidified and was then recrystallized from methanol to give 4.4 g (80%) of white crystal, m.p. 96–97°C. Spectral data: $^1\text{H NMR}$ (CDCl_3) δ 0.10 (s, 9 H), 3.61 (s, 2 H), and 6.70–7.30 ppm (m, 15 H); IR (CCl_4): 3040s, 2990s, 1600s, 1500s, 1400m, 1075m, 1035s, 930w, 820s, 750s and 700s cm^{-1} . MS (m/e , assignment): 376, $P + 1$; 375, P ; 360, $P - \text{CH}_3$; 258, $P - \text{GeMe}_3$; 117, GeMe_3 .

Anal. Found: C, 73.68; H, 7.07. Calcd. for $\text{C}_{23}\text{H}_{26}\text{Ge}$: C, 73.62; H, 6.98%.

Anionic rearrangements

1. *General procedure.* The same general procedure was used for all the anionic rearrangement reactions. *n*-Butyllithium (in *n*-hexane) was slowly added to a solution of the organosilane in anhydrous *N,N,N',N'*-tetramethylethylenediamine or tetrahydrofuran at 0°C (ice-water bath). These highly colored solutions, usually dark red or brown, were stirred at room temperature for different periods of time. The reaction mixtures were hydrolyzed with distilled water or deuterium oxide (99.8%) and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. In every reaction a GLC analysis of the reaction mixture was performed. The products were separated by means of preparative GLC and identified by their NMR, IR, and mass spectra, as well as by elemental analysis.

2. *Rearrangement of 1,1-bis(trimethylsilyl)-1,2-diphenylethane.* *n*-Butyllithium (15.8 ml, 36.72 mmol, 2.3 *N* in *n*-hexane) was added dropwise to a stirred solution of 3.0 g (9.18 mmol) of 1,1-bis(trimethylsilyl)-1,2-diphenylethane in 30 ml of *N,N,N',N'*-tetramethylethylenediamine. Upon the addition of *n*-butyllithium the color of the reaction mixture first turned orange and then dark red after 5 min. After stirring at room temperature for 4 days, the reaction mixture was quenched with distilled water and extracted with ether. The ether layer was washed with 10% aqueous hydrochloric acid to obtain a neutral ether solution, which was dried with magnesium sulfate and concentrated at reduced pressure to a brown oil. GLC analysis (200°C, 6 ft 10% SE-30 on Chromosorb W) showed 5% of 1,2-bis(trimethylsilyl)-1,2-diphenylethane, 90% of 1-[dimethyl(trimethylsilylmethyl)silyl]-1,2-diphenylethane and 5% of starting material. 1,2-Bis(trimethylsilyl)-1,2-diphenylethane was identified by comparison with an authentic sample. The spectral data for 2,2,4,4-tetramethyl-5,6-diphenyl-2,4-disilahexane are as follows: ¹H NMR (neat) δ -0.29 (s, 2 H), 0 (s, 15 H), 2.30 (t, 1 H, *J* = 4 Hz), 3.30 (d, 2 H, *J* = 4 Hz) and 6.72–7.07 ppm (m, 10 H); IR (neat) 3040w, 2945s, 1600m, 1490s, 1450m, 1400m, 1050s, 850s, 750m and 700s cm⁻¹; MS (*m/e*, relative intensity, assignment) 327, 0.4, *P* + 1; 326, 1.6 *P*; 180, 19.6, C₆H₅CH=CHC₆H₅, 145, 100.0, Me₃SiCH₂SiMe₂; 73, 29.1, SiMe₃.

Anal. Found: C, 73.69; H, 9.14. Calcd. for C₂₀H₃₀Si: C, 73.62; H, 9.21%.

The time study of this anionic molecular rearrangement was performed by sampling after intervals of minutes or hours. One milliliter of the reaction mixture was introduced by means of a gas-tight syringe into a test tube containing 0.2 ml of oxygen-free distilled water. The crude oil, obtained by the usual ethereal extraction of the aqueous layer, was subjected to gas chromatographic analysis.

3. *Rearrangement of 1-trimethylsilyl-1,1,2-triphenylethane.* *n*-Butyllithium (13.2 ml, 24.2 mmol, 2.0 *N* in *n*-hexane) was added dropwise to a solution of 1.0 g (3.03 mmol) of 1-trimethylsilyl-1,1,2-triphenylethane in 10 ml of dried *N,N,N',N'*-tetramethylethylenediamine. After stirring at room temperature for 6 days, the reaction mixture was worked up as described above. A brown oil weighing 1.0 g was obtained. This crude oil was subjected to GLC analysis

(230°C, 6 ft 10% SE-30 on chromosorb W). In addition to 41.4% of starting material, and 9.9% of 1,1,2-triphenylethane, 48.74% of 2-trimethylsilyl-1,1,2-triphenylethane appeared as a rearrangement product. The rearrangement product was isolated by means of preparative GLC and identified by comparison of its retention time, IR and NMR spectra with those of an authentic sample.

4. *Attempted rearrangement of 2-trimethylsilyl-1,1,2-triphenylethane.* In accordance with the procedure described above, 0.5 g (1.5 mmol) of this compound was treated with 3.8 ml (6.0 mmol) of *n*-butyllithium in *n*-hexane. The red reaction mixture was stirred at room temperature for 4 days or longer. The crude product (100% recovery) was analyzed by GLC and by its NMR spectrum and was shown to contain only starting material.

5. *Rearrangement of 1-ethyl-1,1,2-triphenylethane.* According to the foregoing procedure, 2.5 g (7.0 mmol) of 1-ethyl-1,1,2-triphenylethane in 20 ml of dry TMEDA was treated with 25.5 ml (56.0 mmol, 2.2 *N* in *n*-hexane) of *n*-butyllithium and stirred at room temperature for six days. After the usual work-up, the resulting crude oil was subject to gas chromatographic analysis (230°C, 6 ft, 10% SE-30 on chromosorb W). In addition to 1,1,2-triphenylethane (2.2%) and starting material (78.5%), a rearrangement product (20.3%) was identified as 2-ethyl-1,1,2-triphenylethane, m.p. 80–81°C. Spectral data: ¹H NMR (CDCl₃) δ 0 (6 H, Me₂Si), 0.23–1.43 (m, 5 H), 3.43 (d, 1 H, *J* = 12 Hz), 4.81 (d, 1 H, *J* = 12 Hz), and 6.9–7.40 ppm (m, 15 H); IR (mineral oil); 1450s, 1250s, 850s, 700s, 650m cm⁻¹; MS: 345, 100, *P* – (C₂H₅); 256, 60, (Ph₂C=CHPh); 87, 100, EtSiMe₂.

Anal. Found: C, 83.79; H, 8.08. Calcd. for C₂₄H₂₈Si: C, 83.65; H, 8.19%.

6. *Attempted rearrangement of 2-trimethylsilyl-1,2-diphenylpropane.* To a solution of 1.5 g (5.6 mmol) of this compound in a 10 ml of dry *N,N,N',N'*-tetramethylethylenediamine was added 9.6 ml of *n*-butyllithium (22.4 mmol, 2.2 *N* in *n*-hexane) at 0°C (ice-water bath). The red suspension was stirred at room temperature for 4 days. Usual work-up afforded 1.45 g of a crude product. Nuclear magnetic resonance and gas chromatographic analysis (6 ft 10% SE-30 on chromosorb W) showed only starting material.

7. *Rearrangement of 1,1-bis(trimethylsilyl)-1-phenylpentane.* 1,1-Bis(trimethylsilyl)-1-phenylpentane (1 g, 3.4 mmol) was treated with 9.1 ml (13.6 mmol, 1.5 *N* in *n*-hexane) of *n*-butyllithium at 0°C (ice-water bath). The red mixture was stirred for 4 days at room temperature, and worked up in the usual way to yield 1.0 g of a crude yellow oil. Gas chromatographic analysis (200°C, at 12 ft 10% SE-30 on Chromosorb W) showed starting material and product in a ratio of 30 : 70. The mixture was separated by means of preparative GLC, and the two fractions were identified by their retention times, IR and NMR spectra: the smaller peak being starting material; the larger constituent, 2,2,4,4-tetramethyl-5-phenyl-2,4-disilanonane, a colorless liquid. Spectral data: ¹H NMR (neat) δ –0.39 (s, 2 H), 0 (s, 15 H), 0.61–2.01 (m, 9 H) and 6.86–7.11 ppm (m, 5 H); IR (neat) 3040w, 2980s, 1600m, 1450m, 1250s, 1050s, 850s, 750s, and 700s cm⁻¹. MS (*m/e*, assignment), 292, *P*; 277, *P* – CH₃; 160,

$\text{Me}_3\text{SiCH}_2\text{SiMe}_3$; 145, $\text{Me}_2\text{SiCH}_2\text{SiMe}_3$; 87, CH_2SiMe_3 .

Anal. Found: C, 69.00, H, 10.91. Calcd. for $\text{C}_{17}\text{H}_{32}\text{Si}_2$; C, 68.83; H, 10.87%.

8. *Rearrangement of 1,1-bis(trimethylsilyl)-1-phenylethane.* In a procedure similar to that above, 1.0 g (4 mmol) of 1,1-bis(trimethylsilyl)-1-phenylethane in 10 ml of dry *N,N,N',N'*-tetramethylenediamine was treated with 8 ml (16 mmol, 2.0 *N* in *n*-hexane) of *n*-butyllithium and stirred for 4 days at room temperature. The NMR spectrum of the brown crude product showed that molecular rearrangement had occurred to an extent of ca. 65%. The rearrangement product was identified as 1-[dimethyl(trimethylsilylmethyl)silyl]-1-phenylethane by an analysis of new NMR spectral peaks, ^1H NMR (neat): δ 0.32 (s, 2 H), 2.05 (t, 1 H, $J = 7$ Hz) and 6.88–7.10 ppm (m, 5 H). Attempts to isolate the rearrangement product from the crude product were unsuccessful.

9. *Rearrangement of 1,2-bis(trimethylsilyl)-1,2-diphenylethane.* According to the foregoing procedure, 200 mg (0.61 mmol) of this compound in 5 ml of dried *N,N,N',N'*-tetramethylethylenediamine was treated with 2 ml (3.6 mmol, 2.26 *N* in *n*-hexane) of *n*-butyllithium. After being stirred 4 days at room temperature, the reaction suspension was hydrolyzed with distilled water. Extraction with ether and removal of solvent gave 0.2 g of a brown oil. Gas chromatography (200°C, 6 ft 10% SE-30 on chromosorb W) of the crude product indicated two main products, starting material and 1-[dimethyl(trimethylsilylmethyl)silyl]-1,2-diphenylethane in the ratio of 83 : 17.

10. *Rearrangement of triphenyl(trimethylsilyl)methane.* Under a nitrogen atmosphere, a solution of 1 g (3.1 mmol) of triphenyl(trimethylsilyl)methane dissolved in 10 ml of dry TMEDA was treated dropwise over 10 min with 5.7 ml (15.5 mmol, 2.2 *N* in *n*-hexane) of *n*-butyllithium with stirring at 0°C (ice-water bath). The blood-red reaction mixture was stirred for 5 days at room temperature and then hydrolyzed with degassed water and worked up in the usual way to give 0.9 g of a crude oil. The crude oil was subjected to gas chromatography (200°C, 6 ft 10% SE-30 on chromosorb W) and four major products were obtained in the ratio 81.0 : 3.7 : 12.2 : 3.1. They were separated by preparative GLC and identified by the standard methods: triphenylmethane (81.0%), 1-diphenylmethyl-2-trimethylsilylbenzene (3.7%), 1-diphenylmethyl-3-trimethylsilylbenzene (12.2%) and 1-diphenylmethyl-4-trimethylsilylbenzene (3.1%).

1-Diphenylmethyl-2-trimethylsilylbenzene: ^1H NMR (CDCl_3) δ 0 (s, 9 H), 5.37 (s, 1 H) and 6.72–7.91 ppm (m, 14 H); IR (neat) 3040w, 2980s, 1600m, 1400m, 1250s, 1120m, 850s, 770s, 700s and 600m cm^{-1} ; MS (*m/e*, relative intensity, assignment) 317, 0.4, $P + 1$; 301, 4.9, $P - \text{Me}$; 243, 1.2, Ph_3C ; 165, 3.9; 135, 5.3, PhSiMe_2 ; 73, 18.6; SiMe_3 .

Anal. Found: C, 84.29; H, 7.78. Calcd. for $\text{C}_{22}\text{H}_{24}\text{Si}$: C, 83.47; H, 7.63%.

1-Diphenylmethyl-3-trimethylsilylbenzene: ^1H NMR (CDCl_3) δ 0 (s, 9 H), 5.70 (s, 1 H) and 6.68–7.13 ppm (m, 14 H); IR (CCl_4) 3040w, 2980s, 2000m, 1600m, 1390m, 1250s, 1120s, 1040s and 850s cm^{-1} ; MS (*m/e*, relative intensity, assignment) 317, 1.7, $P + 1$; 316, 5.7, P ; 301, 9.6, $P - \text{Me}$; 285, 2.5, $P - 2 \text{ Me}$; 243, 2.3, Ph_3C ; 165, 4.6; 150, 0.1, PhSiMe_3 ; 135, 2.8, PhSiMe_2 ; 73, 6.5, SiMe_3 ;

Anal. Found: C, 83.65; H, 7.58. Calcd. for $C_{22}H_{24}Si$: C, 83.47; H, 7.64%.

1-Diphenylmethyl-4-trimethylsilylbenzene: 1H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 5.27 (s, 1 H), and 6.70–7.31 ppm (m, 14 H); IR (neat) 3040w, 2980s, 1500m, 1380m, 1100m, 850s, 750s and 700s cm^{-1} ; MS (m/e , relative intensity, assignment) 317, 1.9, $P + 1$; 316, 6.6, P ; 302, 23.5, $P - Me$; 243, 1.1, Ph_3C ; 165, 3.9; 150, 0.4, $PhSiMe_3$; 73, 7.1, $SiMe_3$.

Anal. Found: C, 83.55; H, 7.76. Calcd. for $C_{22}H_{24}Si$: C, 83.47; H, 7.64%.

11. Rearrangement of 1,2-bis(trimethylsilyl)benzene. To a solution of 300 mg (1.3 mmol) of 1,2-bis(trimethylsilyl)benzene [20] in 5 ml of dry N,N,N',N' -tetramethylethylenediamine (TMEDA) was added 4.92 ml (10.4 mmol, 2.2 N in n-hexane) of n-butyllithium. The red suspension was stirred at room temperature for 5 days. The usual work-up yielded 0.3 g of the crude product which was analyzed by gas chromatography (150°C, 6 ft 10% SE-30 on chromosorb W). Preparative GLC separation of the components revealed the presence of trimethylsilylbenzene, 1,3-bis(trimethylsilyl)benzene, 2,2,4-trimethyl-4-phenyl-2,4-disilapentane, and starting material in the ratio 2.1 : 37.2 : 31.9 : 28.6. The GLC retention time, IR and 1H NMR spectra of each product were compared with those of authentic samples.

12. Attempted rearrangement of 1,3-bis(trimethylsilyl)benzene. From the same procedure as above, the *meta* isomer gave a product containing trimethylsilylbenzene and 1,3-bis(trimethylsilyl)benzene in a ratio of 59.7 : 40.3.

13. Attempted rearrangement of 1,4-bis(trimethylsilyl)benzene. One gram (4.5 mmol) of 1,4-bis(trimethylsilyl)benzene in 10 ml of N,N,N',N' -tetramethylethylenediamine was treated with 8.19 ml (18 mmol, 2.2 N in n-hexane) of n-butyllithium to give a blood-red color in ten min. Stirring at room temperature for 4 days, followed by the usual work-up procedure, gave a crude liquid, 0.97 g. Gas chromatographic analysis (150°C, 6 ft 10% SE-30 chromosorb W) of the crude mixture showed the presence of trimethylsilylbenzene and starting material in the ratio 9.5 : 90.5. Both products were identified by comparison of their retention times and their IR and 1H NMR spectra with those of authentic samples.

14. The cross-over experiments

a) 1,1-Bis(trimethylsilyl)-1-phenylpentane and 1-ethyldimethylsilyl-1,1,2-triphenylethane. An equimolar mixture of 0.36 g (1.25 mmol) of 1,1-bis(trimethylsilyl)-1-phenylethane and 0.42 g (1.25 mmol) of 1-ethyldimethylsilyl-1,1,2-triphenylethane in 5 ml of dry N,N,N',N' -tetramethylethylenediamine was treated with 9.09 ml (20 mmol, 2.2 N in n-hexane) of n-butyllithium. The reaction mixture was stirred at room temperature for 6 days, followed by the usual work-up. The lack of cross-over products was established by gas chromatographic separation of the crude product. Furthermore, the yield of the product resulting from a 1,3-trialkylsilyl group shift was 83.3% for the 1,1-bis(trimethylsilyl)-1-phenylpentane, and 31.0% for a 1,2-trialkylsilyl shift in 1-ethyldimethylsilyl-1,1,2-triphenylethane.

b) 1,2-Bis(trimethylsilyl)-1,2-diphenylethane and 1-trimethylsilyl-1,1,2-tri-

phenylethane. An equimolar mixture of 1,2-bis(trimethylsilyl)-1,2-diphenylethane (0.08 g, 0.25 mmol) and 1-trimethylsilyl-1,1,2-triphenylethane in TMEDA was treated with 1.8 ml of *n*-butyllithium (4 mmol, 2.2 *N* in *n*-hexane). The red reaction mixture was stirred at room temperature for 6 days. Gas chromatographic analysis (6 ft, 10% SE-30 on chromosorb W) of the crude product showed only the individual migration product from the first and second compounds in the ratio of 1.0 : 1.2.

15. *Reactions of diphenyl(trimethylsilyl)methylithium with tetrahydrofuran*. To a solution of 3.6 g (15 mmol) of diphenylmethyl(trimethyl)silane in 75 ml of dry tetrahydrofuran was added 26.4 ml (60 mmol, 2.2 *N* in *n*-hexane) of *n*-butyllithium. After stirring at room temperature for 3 days, another 26.4 ml of *n*-butyllithium was introduced into the reaction mixture and the stirring continued for 3 more days. At the end of this period the reaction mixture was decomposed by addition of distilled water and diethyl ether. The organic layer was separated, washed with water and dried (magnesium sulfate). Removal of solvent under reduced pressure afforded 5 g of brown oil, consisting of three main products as shown by gas chromatography (210°C, 6 ft 10% SE-30 on chromosorb W). They were isolated by preparative GLC and identified as starting material, 3-trimethylsilyl-1,1-diphenylpropane; and 5,5-diphenyl-5-trimethylsilylpentanol, in ratio 39.6 : 28.4 : 32.0.

1,1-Diphenyl-3-trimethylsilylpropane: pale yellow liquid; spectral data: ¹H NMR (CDCl₃) δ 0.00 (s, 9 H), 0.22–0.68 (m, 2 H), 1.82–2.30 (m, 2 H), 3.85 (t, 1 H, *J* = 8 Hz) and 7.08–7.35 ppm (m, 10 H); IR (neat) 3040w, 2980s, 1400m, 1250s, 1160m, 850s and 700s cm⁻¹; MS (*m/e*, relative intensity, assignment): 268, 0.96, *P*; 253, 0.9, *P* – CH₃; 167, 15.0, *P* – (CH₂)₂SiMe₃; 101, 15.0, C₆H₅CH₂C₆H₅; 73, 100, SiMe₃.

Anal. Found: C, 80.59; H, 9.02. Calcd. for C₁₈H₂₄Si: C, 80.57; H, 8.94%.

5,5-Diphenyl-5-trimethylsilylpentanol: viscous pale yellow oil, spectral data: ¹H NMR (CDCl₃) δ 0.00 (s, 9 H), 1.10–1.72 (br, 1 H), 1.90–2.38 (m, 6 H), 3.54 (5, 6 H, *J* = 6 Hz), and 7.20–7.57 ppm (m, 10 H); IR (neat) 3320(br), 3040w, 2970s, 1590m, 1490m, 1390m, 1250s, 1090m, 850s, 750s and 700s cm⁻¹; MS (*m/e*, relative intensity, assignment) 313, 0.8, *P* + 1; 312, 3.9, *P*; 281, 0.6, *P* – CH₂OH; 267, 5.2, *P* – CH₂CH₂OH; 241, 2.0, *P* – (CH₂)₃ – OH; 222, 40.0, *P* – SiMe₂ – OH; 193, 39.8, *P* – CH₂CH₂OH – SiMe₃; 167, 33.3, *P* – (CH₂)₄OH – SiMe₃; 73, 100, SiMe₃.

Anal. Found: C, 76.73; H, 8.97. Calcd. for C₂₀H₂₈SiO: C, 76.86; H, 9.03%.

16. *Attempted rearrangement of 1-trimethylgermyl-1,1,2-triphenylethane*. *n*-Butyllithium (13.2 ml, 24.2 mmol, 2.0 *N* in *n*-hexane) was added dropwise to a solution of 1.0 g (2.66 mmol) of the germanium compound in 10 ml of dried TMEDA. After 6 days at 25°C, usual work-up revealed the presence of starting material and 1,1,2-triphenylethane in a 40 : 60 ratio.

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