The Search for Radical Rearrangement in Organosilicon Systems. I. α-Silyl Radicals from Silaneophyl Systems[1a]

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Abstract: The triphenylsilylmethyl radical (**1**), generated by the di-*t*-butyl peroxide decarbonylation of neat β,β,β-triphenylsilylacetaldehyde (**4**), did not rearrange under the conditions employed. Only triphenylmethylsilane (**10**) resulted. Dilution of **4** in chlorobenzene did not alter the result. This same radical, as well as the phenyldimethylsilylmethyl (silaneophyl) and trimethylsilylmethyl (silaneopentyl) radicals **2** and **3**, respectively, were generated from their corresponding chlorides by means of ethyl Grignard reagent and a small amount of cobaltous chloride (Kharasch–Grignard technique). The reactions proceeded vigorously and high mass balances were obtained in the phenyl cases. Detailed analysis of the products from **1** and **2** indicated that no rearrangement occurred. Both monomeric and dimeric products were unrearranged. From radical **1** resulted **10** (23%) and the dimer 1,1,1,4,4,4-hexaphenyl-1,4-disilabutane (**12**, 72%). From radical **2** came trimethylphenylsilane (**13**, 29%) and the dimer 2,5-dimethyl-2,5-diphenyl-2,5-disilahexane (bisilaneophyl, **15**, 64%). The products from **3** were also unrearranged, *viz.*, tetramethylsilane (**19**, 17%) and the dimer 2,2,5,5-tetramethyl-2,5-disilahexane (**20**, 27%). However, in this case, the volatility of the products reduced the mass balance achieved. Small amounts of ethylated products were also produced in these reactions, coming from ethyl radical capture of the unrearranged α-silyl radicals. A particularly careful search for rearrangement was done in the silaneophyl case. Rearranged monomeric and dimeric products were alternatively synthesized and shown to be absent in the Kharasch–Grignard reaction. The following antirearrangement factors possible in α-silyl radicals are mentioned and discussed: energetics, steric effects, concertedness (push–pull effects), and d_π–p_π electron delocalization (back-bonding).

Little information exists about intramolecular 1,2 rearrangements in silyl radicals. Other than for high-temperature rearrangements (over 400°)[2] and two that form strong silicon–heteroatom bonds,[3] examples of rearrangement in α-silyl radicals have not appeared, although the field is largely unexplored compared to the all-carbon area. Two recent studies,[4] however, have involved the study of α-silyl radicals produced from organometallic precursors. In that by Connolly and Urry,[4a] the reaction of silaneopentyllithium with cobaltous chloride in heptane was investigated and no rearrangement was found. Though a mechanism was not suggested, it is probable that an organocobalt intermediate was involved. A variety of decomposition pathways are available to such species[5] and their chemistry is quite complex. If a silaneopentyl radical were involved, however, it did not rearrange under these conditions. In their report,[4b] published after the completion of the present study, Kumada and coworkers generated both the silaneopentyl and the phenyldimethylsilylmethyl radicals from the corresponding Grignard reagents using silver bromide or chloride. No rearranged products were found, but rather coupling products and products derived from hydrogen abstraction from solvent (ether or ether-containing cumene) were obtained. The coupling products included dimers of the α-silyl radicals (and also bicumyl when cumene was present) as well as products formed by coupling of the α-silyl radical with a solvent-derived radical. This work is very similar to part of what we describe herein. Our findings, while in agreement with those of Kumada and coworkers, extend the search for rearrangement to a more sensitive system (triphenylsilylmethyl) and to another radical process (decarbonylation). Another recent study[6] involved the radical addition of silanes to vinylsilanes, as shown below. The yields of unrearranged products were 41%

$$\mathrm{R_3SiH} \xrightarrow[100^\circ]{\mathrm{Bz_2O_2}} \mathrm{R_3Si}\cdot \xrightarrow{\mathrm{CH_2{=}CHSiR'_3}} \underset{(\alpha\text{-silyl radical})}{\mathrm{R_3SiCH_2\dot{C}HSiR'_3}} \xrightarrow{\mathrm{R_3SiH}} \mathrm{R_3SiCH_2CH_2SiR'_3}$$

with R = R′ = phenyl and 73% with R = phenyl and R′ = *p*-chlorophenyl. Though the authors were not searching for rearrangement, they did note that the reaction mixtures were dark and contained unspecified by-products. From this information one cannot decide definitely, but it would appear that the α-silyl radical intermediate did not rearrange markedly, if at all, under these conditions. With regard to these earlier studies,

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(1) (a) Taken from the M.Sc. thesis of O. K., 1965, and the Ph.D. dissertation of J. F. K., 1968. Portions of this material have appeared in preliminary form: J. W. Wilt and O. Kolewe, *J. Amer. Chem. Soc.*, **87**, 2071 (1965); J. W. Wilt and J. F. Kraemer, Abstracts of Papers, 2nd Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., June 1968, p 39. (b) National Science Foundation Cooperative Graduate Fellow, 1964–1966.

(2) (a) G. Fritz and B. Raabe, *Z. Anorg. Allg. Chem.*, **286**, 149 (1956), suggested a methyl shift from silicon to carbon in an α-silyl radical formed at 580–700°. This seems to be the only claim of a silaneopentyl rearrangement. (b) Radical migration of the trimethylsilyl group from silicon to carbon has been achieved thermally (≤400°) by K. Shiina and M. Kumada, *J. Org. Chem.*, **23**, 139 (1958), and H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 930 (1968), but *not in solution at lower temperatures in the presence of radical initiators*: H. Sakurai, T. Kishida, A. Hosomi, and M. Kumada, *J. Organometal. Chem.*, **8**, 65 (1967).

(3) (a) R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 3848 (1965), describe a presumably radical migration of phenyl from silicon to oxygen. (b) C. G. Pitt and M. S. Fowler, *J. Amer. Chem. Soc.*, **90**, 1928 (1968), report a Kumada-like rearrangement of a silyl group to sulfur in refluxing cyclohexane in the presence of radical initiators.

(4) (a) J. W. Connolly and G. Urry, *Inorg. Chem.*, **2**, 645 (1963); (b) K. Yamamoto, K. Nakamishi, and M. Kumada, *J. Organometal. Chem.*, **7**, 197 (1967).

(5) W. R. Davis and D. B. Denney, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract 131.

(6) C. Eaborn and H. Niederprün, *J. Chem. Soc.*, 797 (1963).

the failure of the silaneopentyl radical (if it is produced in the reactions mentioned[4]) to rearrange is not surprising because the neopentyl radical itself does not do so. However, the addition of radicals to olefins and reactions of the neophyl radical can involve 1,2 rearrangements depending upon the conditions used,[7,8] so the silicon and carbon examples apparently stand apart in these cases.

We felt that an investigation specifically aimed at rearrangement and carried out in rearrangement-prone systems might contribute needed information to this area. Our interest in the radical neophyl rearrangement[8] and its possible heteroatom examples[9] led us, therefore, to look for its silicon analog, *viz.*, the process shown.

$$\underset{\mathbf{1}}{Ph_3SiCH_2\cdot} \xrightarrow{?} \underset{\mathbf{1'}}{Ph_2\dot{\mathrm{Si}}CH_2Ph}$$

The all-carbon process is well documented,[10] but heretofore no study appears extant on this β,β,β-triphenylsilylmethyl radical (**1**). For a bit more breadth, the related phenyldimethylsilylmethyl (for which we have used the term silaneophyl) radical (**2**) and trimethylsilylmethyl (similarly, silaneopentyl) radical (**3**) were also investigated, and our results here add to those already known.[4]

$$\underset{\mathbf{2}}{PhSi(CH_3)_2CH_2\cdot} \qquad \underset{\mathbf{3}}{(CH_3)_3SiCH_2\cdot}$$

As a method for generation of radicals **1**–**3** the decarbonylation of the requisite aldehyde was desirable. Only **1** was so available, however, because of problems encountered in the aldehyde syntheses. Fortunately, the radicals were available from the corresponding chlorides using ethyl Grignard reagent and cobaltous chloride (Kharasch–Grignard technique), a method somewhat different from that used by others in this area.[4]

Results

Syntheses of Starting Materials. Aldehydes **4**–**6** were originally desired for this study. Aldehyde **4** was obtained as described by Eisch and Trainor,[11] but all

$$\underset{\mathbf{4}}{Ph_3SiCH_2CHO} \qquad \underset{\mathbf{5}}{PhSi(CH_3)_2CH_2CHO} \qquad \underset{\mathbf{6}}{(CH_3)_3SiCH_2CHO}$$

attempts to synthesize **5** and **6** led to silicon–carbon cleavage, a facile process in β-ketosilanes,[12] or to rearrangement. These attempts are described briefly in the Experimental Section. For production of radicals **1**–**3** by an alternative method, namely the Kharasch–Grignard reaction, the chlorides **7**–**9** were needed. Chloride **7** was synthesized according to Huang and Wong[13] and chloride **8** by the method of Sommer.[14] Chloride **9** is available commercially.

$$PhMgBr + Cl_3SiCH_2Cl \xrightarrow[61.5\%]{THF} \underset{\mathbf{7}}{Ph_3SiCH_2Cl}$$

$$PhMgBr + ClSi(CH_3)_2CH_2Cl \xrightarrow[80\%]{ether} \underset{\mathbf{8}}{PhSi(CH_3)_2CH_2Cl}$$

$$\underset{\mathbf{9}}{(CH_3)_3SiCH_2Cl}$$

The Decarbonylation of β,β,β-Triphenylsilylacetaldehyde (4). To our knowledge this represents the first decarbonylation of an organosilylaldehyde under radical conditions. Treatment of neat aldehyde **4** at 145–150° with di-*t*-butyl peroxide (DTBP) led to carbon monoxide (50%) and methyltriphenylsilane (**10**, 47% by spectral analysis, confirmed by comparison with known material[15]). Some unreacted **4** (27%) was also present

$$\underset{\mathbf{4}}{Ph_3SiCH_2CHO} \xrightarrow[150^\circ]{DTBP} CO + \underset{\mathbf{10}}{Ph_3SiCH_3}\ (\text{no } \underset{\mathbf{11}}{Ph_2SiHCH_2Ph})$$

together with a small amount of other ill-defined material. *Via* spectral methods able to detect 5% benzyldiphenylsilane (**11**)[16] no evidence was obtained for its presence or possible products therefrom. But silane **11** may be expected to be susceptible to radical disproportionation,[17] and a control experiment showed that indeed about half of it would have been degraded under the reaction conditions employed. In order, then, to test for the presence of the rearranged radical $Ph_2\dot{\mathrm{Si}}CH_2Ph$ (**1′**), the precursor of **11**, advantage was taken of the unique abstraction of aromatic chlorine by silyl radicals.[18] The product of such a reaction, $Ph_2SiClCH_2Ph$, would be easily hydrolyzed and its presence could be tested by titration with base. Thus, when a mixture of silane **11** (1 part), **10** (6 parts), and DTBP were heated in chlorobenzene at 150°, the process proceeded as described, giving 17.9% active chloride (based on the amount of **11** present) by base titration. But when **4** was then decarbonylated with DTBP in chlorobenzene and the crude reaction mixture was taken up in ethanol and titrated potentiometrically with base, only a maximum of 0.2% active chloride was present. Otherwise, only silane **10** (38%) and unchanged **4** (32%) were found.

From all this we conclude that essentially no rearrangement of radical **1** occurred under these conditions, a strikingly different result than that for the β,β,β-triphenylethyl radical which rearranges practically completely under decarbonylation conditions and extensively even in the presence of good hydrogen atom donors.[10] The process with **4** is shown in Scheme I.[19]

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(7) J. Weinstock and E. S. Lewis, *J. Amer. Chem. Soc.*, **79**, 6243 (1957).

(8) J. W. Wilt, L. L. Maravetz, and J. Z. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966), and references therein.

(9) J. W. Wilt and M. P. Stumpf, *ibid.*, **30**, 1256 (1965).

(10) D. Y. Curtin and M. J. Hurwitz, *J. Amer. Chem. Soc.*, **74**, 5381 (1952); D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960); L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

(11) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 2870 (1963).

(12) (a) C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, N. Y., 1960, pp 137–138; (b) A. G. Brook, O. M. McRae, and W. W. Limburg, *J. Amer. Chem Soc.*, **89**, 5493 (1967); (c) *Cf.* J. R. Gold, L. H. Sommer, and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

(13) C. T. Huang and P. J. Wong, *Huu Hsuch Pao*, **25**, 341 (1959); *Chem. Abstr.*, **54**, 16413*d* (1960). The reaction proceeds better in tetrahydrofuran. Use of ethyl ether as mentioned by these authors gave us some chloromethyldiphenylsilanol as well as chloride **7** (see Experimental Section).

(14) L. H. Sommer, *J. Amer. Chem. Soc.*, **76**, 1609 (1954).

(15) R. A. Benkeser, H. Landesman, and D. J. Forster, *ibid.*, **74**, 648 (1952).

(16) H. Gilman and E. A. Zeuch, *ibid.*, **75**, 4560 (1953).

(17) Compare the disproportionation of diphenylsilane with DTBP studied by L. E. Nelson, N. C. Angelotti, and D. R. Weyenberg, *ibid.*, **85**, 2662 (1963).

(18) J. Curtice, H. Gilman, and G. S. Hammond, *ibid.*, **79**, 4754 (1957).

(19) This sequence is the generally accepted course of the peroxide-promoted decarbonylation of aldehydes; see ref 8.

Scheme I

$$\mathrm{DTBP} \xrightarrow{\Delta} 2t\text{-}\mathrm{BuO}\cdot$$

$$\mathrm{Ph_3SiCH_2CHO} + t\text{-}\mathrm{BuO}\cdot \rightarrow \mathrm{Ph_3SiCH_2CO}\cdot + t\text{-}\mathrm{BuOH}$$

$$\mathrm{Ph_3SiCH_2CO}\cdot \rightarrow \mathrm{Ph_3SiCH_2}\cdot + \mathrm{CO}$$

$$\mathrm{Ph_3SiCH_2}\cdot \nrightarrow \mathrm{Ph_2\dot{S}iCH_2Ph}$$

$$\mathrm{Ph_3SiCH_2CHO} + \mathrm{Ph_3SiCH_2}\cdot \rightarrow \mathrm{Ph_3SiCH_3} + \mathrm{Ph_3SiCH_2CO}\cdot$$

The Kharasch–Grignard Reaction with Triphenylsilylmethyl Chloride (7). Considerable controversy exists over the nature of the Kharasch–Grignard reaction[20] Certainly the cobalt sub-halide mechanism originally proposed[20a] is unlikely and some type of finely divided cobalt promoted process seems preferable.[20d,e] Although an *ionic* path is possible[21] a *radical* pathway seems more likely because the rearrangement observed in neophyl systems with this process closely resembles those found in the peroxide-promoted decarbonylation of neophylaldehydes and the decomposition of neophyl peresters, both definitely radical reactions.[20h,22] So, whatever the detailed mechanism, halides do appear to engender radicals as shown. The major product observed is

$$2\mathrm{RX} + 2\mathrm{EtMgX} \xrightarrow{\mathrm{Co^{2+}}} 2\mathrm{R}\cdot + \mathrm{CH_2{=}CH_2} + \mathrm{C_2H_6} + \mathrm{MgX_2}$$

usually the dimer R–R, possibly by a cobalt extrusion process from an organocobalt intermediate as detailed by Tsutsui.[20f] However, in donor solvents, the radical R· may be trapped as R–H. Rearranged monomeric and dimeric products are common in neophyl systems.[20b,h,23]

Reaction of triphenylsilylmethyl chloride (**7**) with ethylmagnesium bromide in tetrahydrofuran at −10 to 0° under nitrogen in the presence of cobaltous chloride, largely as described by Rüchardt and Trautwein[20h] for all-carbon systems, proceeded vigorously. Good temperature control was needed to prevent the reaction from getting out of hand, a situation not encountered with the all-carbon reactions. The products isolated, based on consumed **7**, were methyltriphenylsilane (**10**, 23%) and the symmetrical dimer 1,1,1,4,4,4-hexaphenyl-1,4-disilabutane (**12**, 72%, identical with the known material[6]). Initial chloride **7** was recovered also (31%). The high purity of the dimer **12** as isolated, together with the lack of any spectral evidence for rearranged products, lead us to conclude that radical **1** did not rearrange in the Kharasch–Grignard reaction.

$$\underset{\mathbf{7}}{\mathrm{Ph_3SiCH_2Cl}} \xrightarrow[\mathrm{(CoCl_2)}]{\mathrm{EtMgBr}} \underset{\mathbf{10}}{\mathrm{Ph_3SiCH_3}} + \underset{\mathbf{12}}{\mathrm{Ph_3SiCH_2CH_2SiPh_3}}$$

The Kharasch–Grignard Reaction with Silaneophyl Chloride (8). A more intensive study of products was possible here because they were amenable to gas chromatographic analysis. Reaction of **8** as described above gave a mixture of products which was resolved by a combination of physical and spectral methods. Based on consumed **8** (26% was recovered), the product composition was trimethylphenylsilane (**13**, 29%),[24] phenyldimethyl-*n*-propylsilane (**14**, 6%),[25] and the dimer bisilaneophyl, 2,5-dimethyl-2,5-diphenyl-2,5-disilahexane (**15**, 64%).[26] Because products **14** and **15** were not well defined in the literature,[25,26] they were prepared by the unambiguous routes shown below, giving acceptable analyses and consonant spectra. No rearranged monomeric products such as **16** and/or **17** (see below) were detected, even though 5% of such materials were distinguishable by the analytical methods employed.

$$\underset{\mathbf{8}}{\mathrm{PhSi(CH_3)_2CH_2Cl}} \xrightarrow[\mathrm{(CoCl_2)}]{\mathrm{EtMgBr}} \underset{\mathbf{13}}{\mathrm{PhSi(CH_3)_3}} + \underset{\mathbf{14}}{\mathrm{PhSi(CH_3)_2CH_2CH_2CH_3}} + \underset{\mathbf{15}}{\mathrm{PhSi(CH_3)_2CH_2CH_2Si(CH_3)_2Ph}}$$

$$\mathrm{PhSi(CH_3)_2Cl} + n\text{-}\mathrm{PrMgBr} \xrightarrow[79.5\%]{\text{ether}} \mathbf{14}$$

$$\mathrm{PhSi(CH_3)_2H} + \mathrm{CH_2{=}CHSi(CH_3)_2Ph} \xrightarrow[71.5\%]{\mathrm{H_2PtCl_6}} \mathbf{15}$$

To check product stability, benzyldimethylsilane (**16**)[27] was prepared and shown to be largely unaffected by reaction conditions. Some 93.5% of **16** introduced into the reaction with **8** in a control experiment was recoverable, with the remainder being mainly ethylated to benzyldimethylethylsilane (**17**),[28] which product also resulted in low yield upon treatment of **16** itself with ethyl Grignard reagent and cobaltous chloride. The structure was confirmed by the alternative synthesis shown.

$$\underset{\mathbf{16}}{\mathrm{PhCH_2Si(CH_3)_2H}} \xrightarrow[\substack{\mathrm{(CoCl_2)}\\ 6\text{–}7\%}]{\mathrm{EtMgBr}} \underset{\mathbf{17}}{\mathrm{PhCH_2Si(CH_3)_2Et}} \xleftarrow[45\text{–}60\%]{\mathrm{EtMgBr}} \mathrm{PhCH_2Si(CH_3)_2Cl}$$

In the search for possible rearranged dimeric products, one of the possible rearranged dimers was prepared, *viz.*, the half-rearranged dimer 2,2,4-trimethyl-1,4-diphenyl-2,4-disilapentane (**18**).[29] Lithiomethyldimethylphenylsilane was synthesized by the method of Fritz and Burdt[30] and condensed with benzyldimethylchlorosilane to

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[20] (a) M. S. Kharasch and E. K. Fields, *J. Amer. Chem. Soc.*, **63**, 2316 (1941); (b) W. H. Urry and M. S. Kharasch, *ibid.*, **66**, 1438 (1944); (c) A. L. Wilds and W. B. McCormack, *J. Org. Chem.*, **14**, 45 (1949); (d) W. B. Smith, *ibid.*, **24**, 703 (1959); (e) F. W. Frey, Jr., *ibid.*, **26**, 5187 (1961); (f) M. Tsutsui, *Ann. N. Y. Acad. Sci.*, **93**, 133 (1961); *Chem. Abstr.*, **57**, 16653 (1962); (g) L. H. Slaugh, *J. Amer. Chem. Soc.*, **83**, 2734 (1961); (h) C. Rüchardt and H. Trautwein, *Chem. Ber.*, **96**, 160 (1963); (i) D. T. Davies, D. H. Hey, and M. Tiecco, *J. Chem. Soc.*, 7062 (1965).

[21] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 270.

[22] C. Rüchardt and R. Hecht, *Chem. Ber.*, **98**, 2460 (1965).

[23] W. H. Urry and N. Nicolaides, *J. Amer. Chem. Soc.*, **74**, 5163 (1952).

[24] C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

[25] N. S. Nametkin, V. M. Vdovin, P. L. Grinberg, and E. D. Babich, *Dokl. Akad. Nauk SSSR*, **161**, 358 (1965); *Chem. Abstr.*, **63**, 625*b* (1965). Little data was given in the abstract, however, and **14** was authenticated *via* synthesis (see text).

[26] C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956), reported this compound as a waxy solid that fluoresced under uv light, mp >100°, from the phenylation of silane **13** (presumably a coupling product). From our results we suspect their compound was not the dimer **15**. The authors found their compound to be difficultly purified and did not characterize it further. Very recently, Kumada, *et al.*,[4b] reported the compound as a crystalline solid, mp 60°, in good agreement with our data.

[27] J. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 552 (1950).

[28] C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, **3**, 168 (1965), isolated this compound as a by-product of another reaction. They gave no physical constants and we confirmed our product again, therefore, by an alternative synthesis (see text).

[29] Only phenyl-shifted products were considered because phenyl migrated rather than methyl in the *ionic* rearrangement of chloride **8** [R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometal. Chem.*, **3**, 455 (1965)]. No work was done on the *fully rearranged* dimer because initially we felt rearrangement would be slight and dimerization of two such rearranged radicals would be therefore very remote. As it turned out, not even dimer **18** seems to be formed.

[30] G. Fritz and H. Burdt, *Z. Anorg. Allg. Chem.*, **314**, 35 (1962).

Table I. Kharasch–Grignard Reactions

$$R_3SiCH_2Cl \xrightarrow{EtMgBr,\ CoCl_2} products$$

Halide	R	Product, %[a] R$_3$SiCH$_3$	R$_3$SiCH$_2$CH$_2$SiR$_3$	R$_3$SiCH$_2$CH$_2$CH$_3$
7	Ph	**10**, 23	**12**, 72	*b*
8	Ph, (CH$_2$)$_3$	**13**, 29	**15**, 64	**14**, 6
9	CH$_3$	**19**, 17	**20**, 27	**21**, trace

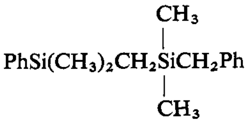
[a] Based on consumed initial chloride. [b] Less excess ethyl bromide (used to prepare the Grignard reagent) was present in the case of **7**. There were, therefore, fewer ethyl radicals available to combine with radical **1** to give triphenyl-*n*-propylsilane (**22**)[43] as a product. Though its presence was not demonstrated, **22** could conceivably have been produced in very small amount.

afford **18**, a high-boiling oil easily differentiable spectrally from **15** (Scheme II). Indeed dimers **18** and **15** could be detected in the *mixed* Kharasch–Grignard reaction of **8** and **16** mentioned earlier. Significantly, however, dimer **15** was quite pure as isolated from the Kharasch–Grignard reaction of **8** itself (no **16** present), indicating the absence of rearranged dimers. This absence, together with the absence of rearranged monomeric products **16** and/or **17**, leads us to conclude that radical **2**, like **1**, does not rearrange under these conditions. Kumada and coworkers[4b] in a similar study reported no rearrangement also. They observed formation of **13** and **15** together with (2-ethoxypropyl)phenyldimethylsilane. This last is a coupling product of radical **2** and an ether-derived radical.

Scheme II

$$PhSi(CH_3)_2CH_2Cl \xrightarrow[2.\ HgCl_2]{1.\ Mg,\ ether} [PhSi(CH_3)_2CH_2]_2Hg \xrightarrow[ether]{Li} PhSi(CH_3)_2CH_2Li$$

$$PhSi(CH_3)_2CH_2Li + ClSi(CH_3)_2CH_2Ph \xrightarrow[76\%]{ether}$$



$$PhSi(CH_3)_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}CH_2Ph$$

18

Because neophyl chloride has been thoroughly studied in this reaction,[20b,h] (indeed, the neophyl rearrangement was discovered in this way[20b]) we thought it prudent to check our procedures on this chloride. We were able to duplicate the recent data of Rüchardt and Trautwein[20h] quite well, finding 33% rearrangement compared to their 33.6% rearrangement.

The Kharasch–Grignard Reaction with Silaneopentyl Chloride (9). Connolly and Urry in 1963 reported the reaction of lithiomethyltrimethylsilane with cobaltous chloride in heptane.[4a] Only tetramethylsilane (**19**) and the dimer **20**[31] were reported products and no mechanism was suggested. Our results on **9** were essentially the same. Its treatment with ethyl Grignard reagent and cobaltous chloride led to **19** (17%) and **20** (27%), again based upon consumed **9**, 17% of which was recovered. There was also a trace amount of trimethyl-*n*-propylsilane (**21**) produced. The poorer yields in this case compared to those from **7** and **8** reflect the experimental problems encountered with these volatile compounds. The products were verified by comparison with authentic materials separately obtained. No evidence for rearrangement was found and we conclude that radical **3** also does not rearrange under these conditions. Likewise Kumada, *et al.*,[4b] found no rearrangement in their study of radical **3**. Silanes **19** and **20** were observed as well as a coupling product of **3** with an ether-derived radical.

$$\underset{\mathbf{9}}{(CH_3)_3SiCH_2Cl} \xrightarrow[(CoCl_2)]{EtMgBr} \underset{\mathbf{19}}{(CH_3)_3SiCH_3} + \underset{\mathbf{20}}{(CH_3)_3SiCH_2CH_2Si(CH_3)_3} + \underset{\mathbf{21}}{(CH_3)_3SiCH_2CH_2CH_3}$$

Summary. The results with halides **7–9** are gathered in Table I. All the processes may be shown by the same series of reactions as indicated in Scheme III.

Scheme III

$$R_3SiCH_2Cl \xrightarrow[(CoCl_2)]{EtMgBr} R_3SiCH_2\cdot + \ldots$$

$$R_3SiCH_2\cdot \underset{H\text{-}solvent}{\not\longrightarrow} R_2\dot{S}iCH_2R$$

$$R_3SiCH_2\cdot \longrightarrow R_3SiCH_3 + (solvent)\cdot$$

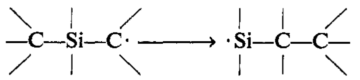
$$2R_3SiCH_2\cdot \longrightarrow R_3SiCH_2CH_2SiR_3$$

$$R_3SiCH_2\cdot \xrightarrow[(from\ EtMgBr)]{Et\cdot} R_3SiCH_2CH_2CH_3$$

Discussion

The present results add to the little previously known about α-silyl radicals.[32] The obvious question is why these α-silyl radicals do not rearrange while their carbon counterparts often do. Several factors may be involved in this lack of rearrangement ("antirearrangement" factors) and each will be discussed in turn. We restrict this discussion to the situation where the potential migrating group and the terminus are carbon, because rearrangement of other α-silyl radicals is known.[2,3]

1. Energetics. Only a qualitative view of this feature is possible with the available data. The transformation



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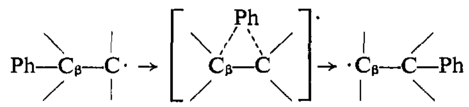
(31) D. N. Andreev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 237 (1960); *Chem. Abstr.*, **54**, 2084*f* (1960).

(32) Neither Eaborn[12] nor L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, mention such species.

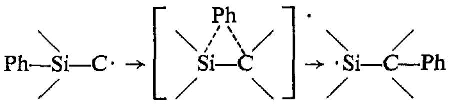
breaks a weaker Si–C bond (69–76 kcal $\mathrm{mol^{-1}}$)[33] and forms a stronger C–C bond (83 kcal $\mathrm{mol^{-1}}$).[33] On this basis the rearrangement seems enthalpically possible. Of course, neither the over-all free-energy change nor, more importantly, the activation energy for this process seems calculable at this time. Moreover, silyl radicals seem less stable and more reactive than their carbon counterparts. For instance, hexaphenyldisilane does not dissociate[34] as does hexaphenylethane and triphenylsilyl radical dechlorinates chlorobenzene,[18] an unknown reaction for triphenylmethyl radical. In balance, the inherent instability of the silyl radical as a whole may decrease the favorable ΔH value seen above as a consequence of only the C–C bond content. As a result it remains unsettled to us as to whether energetics favors the process. Certainly under the conditions studied here, other reactions were *more* energetically favored. Interestingly, the reverse rearrangement did *not* occur in the benzyldimethylsilyl radical.[35]

2. **Steric Effects.** The greater covalent bond radius of silicon (1.17 Å) compared to carbon (0.77 Å)[36] means that less β-steric compression exists in radicals **1** and **2** compared to the carbon species. Because increased β compression assists,[37] but is not necessary for,[38] radical rearrangement, the lack of it may explain the present results. In the potential migrating phenyl group the farther removal of its π cloud in **1** and **2** from the orbital of the unpaired electron would require increased deformation of these radicals to achieve the overlap required to initiate rearrangement.

Another steric effect may be mentioned. The $\mathrm{Ar_1}$-3 state used in the neophyl radical rearrangement[37] produces a cyclopropane-like activated complex, as shown.

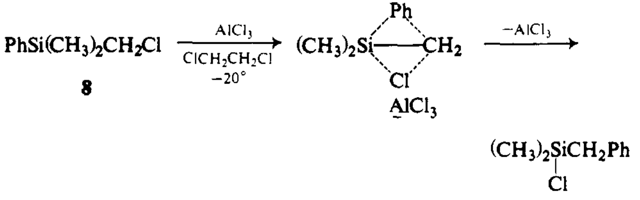


A similar activated complex for the radicals **1** and **2**, shown below, would involve considerably more strain.

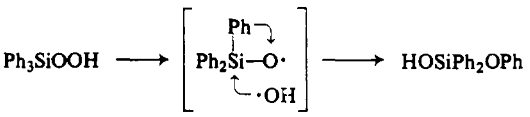


Using normal bond lengths, the Ph–Si–C angle in the complex would be *ca.* 48°, considerably less than the *ca.* 60° involved in the neophyl radical. Silacyclopropanes are unknown,[39] reflecting this increased strain over cyclopropanes, and this increased strain could well preclude a facile 1,2 rearrangement of this type.

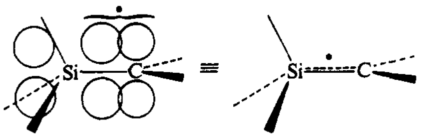
3. **Push–Pull Effect.** 1,2 shifts are, of course, well known in silicon systems and the above steric argument may seem refuted thereby. But evidence indicates that these 1,2 shifts are in some (and perhaps all) cases really concerted or stepwise push–pull processes of considerably different mechanism than the superficially analogous carbon 1,2 shifts. For example, the recent conversion of **8** to benzyldimethylchlorosilane has been viewed in this way by Eaborn and coworkers.[29]



The interesting Wieland-type rearrangement observed by Dannley and Jalics[3a] also may be viewed as a push–pull recombination process in a solvent cage. Many details of such reactions are as yet unclear, but the participation of the 3d silicon orbitals undoubtedly changes the bond angles in these complexes and vitiates any exact comparison of them to all-carbon analogies. Nevertheless, if such a push–pull mechanism is *required* for silicon systems, neither the decarbonylation nor Kharasch–Grignard processes studied here would seem amenable to such a pathway.



4. **Back-Bonding ($\mathrm{d_\pi}$–$\mathrm{p_\pi}$ Bonding).**[40] This phenomenon is well documented for silylamines and other silicon compounds containing the $\equiv\mathrm{Si\ddot{G}}$ moiety.[41] We suggest as an additional reason for the lack of rearrangemet in the radicals studied here precisely such a delocalization of the unpaired electron into a $3\mathrm{d}_\varepsilon$ orbital of silicon (the $3\mathrm{d}_{xz}$ is shown). Such an effect would stabilize the radical and reduce the driving force for rearrangement. Although such back-bonding has not, to our knowledge, been suggested for α-silyl radicals, it does rationalize the data well. It is also interesting to speculate whether in $\mathrm{Ph_3Si\text{–}\ddot{O}\cdot}$ and the sulfur analog the back-bonding of the oxygen or sulfur n electrons into two of the three d_ε silicon orbitals eliminates the potential *unpaired* electron stabilization and allows the Wieland-type rearrangements to occur,[3] albeit probably by a push–pull pathway. Also, α-silyl cations could not be so stabilized and their noted rearrangement would not then be prohibited.



Further work on organosilicon radical rearrangements is continuing.

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(33) L. H. Sommer, ref 32, p 25. More recent values for D(Si–C) are 83–85 kcal $\mathrm{mol^{-1}}$ [G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, **87**, 5327 (1965)]. If these values are correct, then the rearrangement under discussion would seem to be thermoneutral.

(34) T. C. Wu and H. Gilman, *J. Org. Chem.*, **23**, 913 (1958).

(35) Nelson, *et al.*,[17] found no rearrangement (or disproportionation) of benzyldimethylsilane. Also, we found only unrearranged products from the Kharasch–Grignard reaction of benzyldimethylchlorosilane (see Experimental Section).

(36) L. H. Sommer, ref 32, p 176.

(37) J. W. Wilt and H. Philip, *J. Org. Chem.*, **25**, 891 (1960).

(38) L. H. Slaugh, *J. Amer. Chem. Soc.*, **81**, 2262 (1959); W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 29 (1964).

(39) Eaborn, ref 12a, pp 370–371, summarizes attempts at their synthesis.

(40) We use this term in a somewhat different sense than that originated by M. J. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951). In the latter, a transition metal ion was postulated to bond to an olefin *via* a σ bond between the π electrons of the olefin and an empty s metal ion orbital as well as by a π bond between a filled d metal ion orbital and the empty π* orbital of the olefin.

(41) See Eaborn, ref 12a, pp 94–98.

Experimental Section

Melting and boiling points are uncorrected for stem exposure. The former were taken on a calibrated Fisher-Johns block. Spectra were determined on Perkin-Elmer Model 21, Beckman IR-5A, and Varian A-60 or A-60A instruments. Spectra taken on the first two (infrared) were either on the neat material, on 3% solutions in chloroform, or as potassium bromide disks. Infrared absorptions are given in microns. Only significant absorptions are listed. Spectra taken on the last two instruments (nmr) were usually on samples dissolved in carbon tetrachloride, neat, or in chloroform-*d*. The references used were external tetramethylsilane (ext TMS), internal tetramethylsilane, 1% (int TMS), or internal *p*-dioxane (1%) centered at δ 3.7 (int dioxane). The chemical shift values are given in parts per million (δ units). Unless the range is given, the δ values of multiplets are centers. Pertinent protons are italicized when required. The splitting symbols used are s, singlet; d, doublet, etc. Gas chromatographic analysis (glpc) was performed on an Aerograph A-90-P machine, using helium as the carrier gas at 60 cc min^{-1}. Signals were recorded on a Sargent Model SR-GC 1-mV recorder equipped with a disk integrator. Microanalyses were conducted by Micro-Tech Laboratories, Inc., Skokie, Ill., and by M-H-W Laboratories, Garden City, Mich. All critical solvents were purified to glpc homogeneity. The procedures given are typical, though in some preparations the exact details varied slightly.

Decarbonylation Study. Materials. Triphenylsilylacetaldehyde (4) was synthesized in 40% yield by the method of Eisch and Trainor[11] with the following modifications. Ethyl ether was used instead of *n*-butyl ether and magnesium bromide etherate was made using ethylene bromide (rather than bromine) on the metal in ether. The aldehyde was a white solid, mp 110–112°, lit.[11] mp 115.5–116°, and the ir and nmr spectra agreed with those reported. **Methyltriphenylsilane (10)** was prepared in the usual fashion from triphenylchlorosilane and methylmagnesium bromide [60%; mp 68–69°; λ^{CHCl_3} 7.95 (SiCH_3) μ; $\delta^{\text{CDCl}_3}_{\text{int TMS}}$ 7.38 m (ArH), 0.83 s (CH_3); lit.[15] mp 68.5–69°]. **Benzyldiphenylsilane (11)** was obtained by the method of Gilman and Zuech[16] [71%; mp 38–39°; λ^{CHCl_3} 4.68 (SiH) μ; $\delta^{\text{CDCl}_3}_{\text{int TMS}}$ 7.35 m, 7.05 m (ArH), 4.93 t (SiH, J = 3.5 Hz), 2.65 d (CH_2); lit.[16] bp 140–143° (0.1 mm)].

Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{Si}$: C, 83.15; H, 6.61. Found: C, 83.32; H, 6.63.

Decarbonylation of 4. The molten aldehyde (0.66 g, 2.2 mmol) was treated under nitrogen with several injections of di-*t*-butyl peroxide (DTBP, redistilled, total 0.32 g, 2.2 mmol) over 2.5 hr at 145–150° in a reflux apparatus. The evolved gas was collected over water and subsequently analyzed for carbon monoxide in a Fisher dual-column gas partitioner (27.6 cc of CO, 49.7%). The red reaction material was then concentrated under vacuum to an oily residue (0.6 g) which was diluted to 10 ml with carbon tetrachloride. Infrared analysis of this solution was then performed using calibration data (absorbance *vs.* concentration) from pure compounds in carbon tetrachloride and correcting for interferences in mixtures of them at certain diagnostic absorptions:[42] 4.7 μ for SiH (**11**), 5.85 for CH=O (**4**), and 8.05 for SiCH_3 (**10**). The analysis indicated 26.8% recovered **4** and 46.8% **10**. No evidence for **11** was found. The carbon tetrachloride solution was then freed of solvent and chromatographed on Florisil. Pentane and benzene eluted **10** (confirmed spectrally, 0.42 g, slightly contaminated with DTBP, **4**, and a hydroxy compound, probably triphenylsilanol), while chloroform eluted some ill-defined material showing phenylsilicon ir absorption (0.05 g).

A similar decomposition of **4** (0.53 g, 1.75 mmol) in refluxing chlorobenzene (3.52 g) using DTBP (1.9 mmol) in several injections over 3.5 hr led to **10** (38%) and recovered **4** (32%), again by ir analysis as above. Volatile material was removed under vacuum and the residue was dissolved in 95% ethanol and then diluted with pure water. Micropotentiometric titration of this solution with 0.02 *N* NaOH indicated, after correction for a blank done as above but omitting **4**, that 0.15 ± 0.05% chloride ion was present.

Control Studies. A solution of DTBP (0.39 g, 2.61 mmol) and **11** (0.062 g, 0.22 mmol) was heated at 145–150° for 5 hr. The mixture was diluted with carbon tetrachloride to 10 ml and the infrared spectrum taken. Analysis indicated *ca.* 48% of **11** had been destroyed in the process.

A mixture of **11** (0.05 g, 0.195 mmol), **10** (0.324 g, 1.18 mmol), and DTBP (0.45 g, 3.07 mmol) was refluxed in chlorobenzene (3.4 g) for 4 hr. Removal of solvent and micropotentiometric titration of the residue in alcohol–water as before with 0.2 *N* NaOH indicated 17.9% chloride ion was present.

The potentiometry was corrected in all these studies *via* a blank determination on a mixture of DTBP (0.4 ml) and chlorobenzene (3 ml) heated under reflux for 3.5 hr.

Kharasch–Grignard Reaction with Triphenylsilylmethyl Chloride (7). Materials. Chloride **7** was prepared by the method of Huang and Wong[13] [61.5%; mp 113–114°; λ^{KBr} 3.33, 3.47 (CH), 7.03, 9.02 (PhSi), 13.55, 13.72, 14.12, 14.35 μ; $\delta^{\text{CCl}_4}_{\text{int TMS}}$ 7.25–7.75 m (ArH), 3.42 s (CH_2Cl); lit.[13] mp 113–114°]. **Methyltriphenylsilane (10)** was obtained as described[15] [81%; mp 65.5–67°; λ^{KBr} 3.3, 3.5 (CH), 7.05, 9.05 (PhSi), 8.06, 12.68 (CH_3Si), 13.6, 13.66, 13.89, 14.36 μ; $\delta^{\text{CCl}_4}_{\text{int dioxane}}$ 7.33–7.87 m (ArH), 0.97 s (CH_3Si); lit.[15] mp 65.5–66.5°]. **Triphenyl-*n*-propylsilane (22)** was synthesized by the literature method[43] [56%; mp 84–85°; λ^{KBr} 3.3, 3.44, 3.53 (CH), 7.04, 9.05 (PhSi), 8.5, 8.7, 9.4, 10.04, 12.6, 13.46, 13.8, 14.35, 15.1 μ; $\delta^{\text{CCl}_4}_{\text{int TMS}}$ 7.1–7.7 m (ArH), 1.2–1.8 m ($\text{CH}_3\text{C}\mathit{H}_2\text{C}\mathit{H}_2\text{Si}$), 1.0 t ($\text{C}\mathit{H}_3\text{CH}_2\text{CH}_2\text{Si}$); lit.[43] mp 84°]. **1,1,1,4,4,4-Hexaphenyl-1,4-disilabutane (12)** was made by adding four drops of chloroplatinic acid (0.12 *M* in ethanol) to a solution of triphenylsilane (1 g, 3.85 mmol, mp 33–35°, lit.[44] mp 43–44°) and triphenylvinylsilane (1.1 g, 3.85 mmol, mp 67–70°, lit.[45] 72°) in ligroin (bp 90–120°, 10 ml). The mixture was heated under reflux for 23 hr and chilled and the precipitated solid (1.62 g, 77%) was collected. Recrystallization from tetrahydrofuran–ether afforded **12** as white crystals [1.4 g; mp 216–217°; λ^{KBr} 3.31, 3.48 (CH), 7.05, 9.04 (PhSi), 14.1, 14.4 μ; $\delta^{\text{CDCl}_3}_{\text{int TMS}}$ 7.1–7.7 m (ArH), 1.5 s (CH_2CH_2); lit.[6] mp 216–217°] made by peroxidic promotion of the above addition.

Attempted Rearrangement of 7. All operations prior to hydrolysis were done under nitrogen. Ethylmagnesium bromide (0.05 mol) was prepared in dry tetrahydrofuran (freshly distilled from lithium aluminum hydride, 15 ml). Chloride **7** (15.44 g, 0.05 mol) in further dry tetrahydrofuran (33 ml) was then added to the Grignard solution at −10°. Anhydrous cobaltous chloride (0.21 g, 1.55 mmol) was added next, causing the mixture to turn black and to evolve gas after a short induction period. After the gas evolution subsided, the mixture was refluxed for 2.75 hr. Hydrolysis of the cooled solution was achieved with dilute acetic acid (10%, 30 ml). Additional water (50 ml) was then added, followed by ether (400 ml) with stirring. The ether phase, which contained suspended solid, was carefully separated, washed well with saturated sodium bicarbonate solution and water (50 ml each), and then filtered free from the suspended solid. This solid (6.6 g, mp 214.5–215.5°) proved to be the dimer **12** by spectral and mixture melting point comparison with authentic material. The filtrate was clarified with a small portion of tetrahydrofuran and dried over sodium sulfate. Upon refrigeration overnight an additional 0.2 g of **22** precipitated. The solution was evaporated to dryness to yield a pale yellow solid (8.4 g). From nmr calibration data obtained from known mixtures this solid consisted of unreacted **7** (4.8 g, 31% recovery), silane **10** (2.23 g), and some odorous byproduct that was not identified (1.37 g). We suspect this is a siloxane derived from **7** by cleavage. Calculations then gave the product composition as given in Table I, with the odorous byproduct amounting to 4.2% of the consumed **7**. No evidence was found for rearranged structures, nor for ethylation of **7** to form **22**. As little as 5% of **22** was detectable by nmr analysis in mixtures of the other products.

Kharasch–Grignard Reaction with Silaneophyl Chloride (8). Materials. Chloride **8** was prepared as described by Sommer[14] [80.5%; bp 74–75° (0.35 mm); λ^{neat} 3.3–3.5 (CH), 7.0, 9.0 (PhSi), 8.0 (CH_3Si) μ; $\delta^{\text{neat}}_{\text{ext TMS}}$ −0.2 s (CH_3Si), 2.25 s (CH_2Cl), 6.85 m (ArH); lit.[14] bp 135° (48 mm)]. **Trimethylphenylsilane (13)** was obtained in straightforward fashion by reducing **8** *via* its Grignard reagent and water [75%; bp 168–171° (752 mm); λ^{neat} 3.3–3.5 (CH), 7.0, 9.0 (PhSi), 8.0, 11.85 (CH_3Si) μ; $\delta^{\text{neat}}_{\text{ext TMS}}$ 6.83 m (ArH), −0.33 s (CH_3Si); lit.[24] bp 171.5 (atm)]. **Benzyldimethylsilane (16)** resulted from treatment of benzyldimethylchlorosilane (Pierce Chemical Co., Rockford, Ill.) with lithium aluminum hydride in ether according to the method of Russell[46] for another compound

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(42) For the many details of this analysis, the thesis of O. K. should be consulted.

(43) H. Gilman, A. Brook, and L. Miller, *J. Amer. Chem. Soc.*, **75**, 3753 (1953).

(44) H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).

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

(46) G. A. Russell, *ibid.*, **21**, 1190 (1956).

[67.5%; bp 41–42° (1.5 mm); $n^{16}\mathrm{D}$ 1.5035; $d^{26}{}_4$ 0.8707; λ^{neat} 3.3–3.5 (CH), 4.7 (SiH), 8.0, 11.3 ($\mathrm{CH_3Si}$) μ; $\delta^{\mathrm{CCl_4}}_{\text{int dioxane}}$ 7.2 m (ArH), 4.13 nonet (SiH, $J(\mathrm{SiHCH_3}) = J(\mathrm{SiHCH_2}-)$ = 3.4 Hz), 2.25 d ($\mathrm{CH_2Si}$), 0.12 d ($\mathrm{CH_3Si}$); lit.[27] bp 53–55° (3 mm); $n^{20}\mathrm{D}$ 1.5040; $d^{20}{}_{20}$ 0.9486]. **Benzyldimethylethylsilane (17)** was synthesized by reaction of ethylmagnesium bromide (0.063 mol) with benzyldimethylchlorosilane (11.5 g, 0.063 mol) in ether (50 ml) with stirring at 25° for 11 hr. Processing the reaction in the usual way led to **17** as a colorless oil [8.12 g; 45.5%; bp 54–55° (0.75 mm); $n^{22}\mathrm{D}$ 1.4962; $d^{26}{}_4$ 0.8797; λ^{neat} 3.35, 3.43–3.5 (CH), 8.05, 12.0 ($\mathrm{CH_3Si}$) μ; $\delta^{\mathrm{CCl_4}}_{\text{int dioxane}}$ 7.0–7.4 m (ArH), 2.2 s ($\mathrm{PhC}H_2$), 1.1 t ($\mathrm{C}H_3\mathrm{CH_2Si}$), 0.6 q ($\mathrm{CH_3C}H_2\mathrm{Si}$), 0.1 s ($\mathrm{CH_3Si}$)].

Anal. Calcd for $\mathrm{C_{11}H_{18}Si}$: C, 74.09; H, 10.17. Found: C, 73.91; H, 10.53.

Phenyldimethyl-*n*-propylsilane (14) was made similarly through reaction of *n*-propylmagnesium bromide (0.15 mol) and phenyldimethylchlorosilane (Pierce Chemical Co., Rockford, Ill., 17 g, 0.1 mol) in ether (75 ml) under reflux for 25 hr. The normal work-up led to **14** as a colorless oil [14.1 g; 79.5%; bp 52–55° (0.7 mm); λ^{neat} 3.3, 3.35, 3.4, 3.45 (CH), 7.02, 9.0 (PhSi), 8.04, 12.0 ($\mathrm{CH_3Si}$) μ; $\delta^{\mathrm{CCl_4}}_{\text{int dioxane}}$ 7.3–7.8 m (ArH), 1.8–0.7 m (n-$\mathrm{C_3H_7Si}$), 0.4 s ($\mathrm{CH_3Si}$)].

Anal. Calcd for $\mathrm{C_{11}H_{18}Si}$: C, 74.09; H, 10.17. Found: C, 73.58; H, 9.96.

2,5-Diphenyl-2,5-dimethyl-2,5-disilahexane (Bisilaneophyl, 15). Preparation was effected by adding three drops of chloroplatinic acid (0.12 *M* in ethanol) to a neat mixture of phenyldimethylvinylsilane (Pierce, 1 g, 6.15 mmol) and phenyldimethylsilane (prepared as described[46] in 80% yield, 2.38 g, 18 mmol). The mixture turned green and became hot, so cooling was applied. After this initial reaction the reaction was heated at 100° for 17 hr and then distilled free of excess phenyldimethylsilane (bp *ca.* 25° at 0.55 mm). The viscous residue solidified when scratched and was recrystallized from petroleum ether (bp 30–60°) with the use of decolorizing carbon to give **15** as a white crystalline solid [1.3 g; 71.5%; mp 57.5–58°; λ^{KBr} 3.3–3.5 (CH), 7.0, 9.0 (PhSi), 8.05, 12.05 ($\mathrm{CH_3Si}$), 8.85, 9.5, 12.25, 13.0, 13.55, 14.25 μ; $\delta^{\mathrm{CCl_4}}_{\text{int dioxane}}$ 7.3–7.7 m (ArH), 0.82 s ($\mathrm{CH_2CH_2}$), 0.45 s ($\mathrm{CH_3Si}$); lit.[4b] mp 60°].

Anal. Calcd for $\mathrm{C_{18}H_{26}Si_2}$: C, 72.42; H, 8.78. Found: C, 71.93; H, 8.89.

2,2,4-Trimethyl-1,4-diphenyl-2,4-disilapentane (Half-Rearranged Dimer, 18). Lithiomethyldimethylphenylsilane was prepared by the method of Fritz and Burdt.[30] To this organometallic (0.12 mol) in dry ether (160 ml) was added benzyldimethylchlorosilane (22.2 g, 0.12 mol) in ether (10 ml) with stirring and under nitrogen. Reflux occurred during the addition and a white precipitate formed. After the addition the mixture was heated under reflux for 4.5 hr and then hydrolyzed with water (50 ml). The layers were separated and the aqueous layer was extracted with two 25-ml portions of ether. The combined ether solutions were washed with water, dried, and evaporated. The residual oil was distilled to afford **18** as an oil that resisted solidification even at −80° [27.18 g, 76%, bp 153–158° (0.75–1.75 mm)]. The analytical sample was redistilled [bp 115° (0.01 mm); $n^{21}\mathrm{D}$ 1.5438; $d^{27}{}_4$ 0.963; λ^{neat} 3.28, 3.33, 3.41 (CH), 7.02, 9.00 (SiPh), 8.02, 12.20 ($\mathrm{CH_3Si}$), 8.30, 8.67, 9.23, 12.00, 12.33, 13.14, 13.7, 14.35 μ; $\delta^{\text{neat}}_{\text{int TMS}}$ 6.7–7.6 m (ArH), 1.93 s ($\mathrm{PhC}H_2\mathrm{Si}$), 0.22 s ($\mathrm{PhSi(C}H_3)_2-$), −0.1 s ($\mathrm{SiCH_2Si}$ and $\mathrm{PhCH_2Si(C}H_3)_2-$); in benzene as a 50% solution, the $\mathrm{SiCH_2Si}$ resonance changed to δ 0.0 s while the others were unchanged].

Anal. Calcd for $\mathrm{C_{18}H_{26}Si_2}$: C, 72.42; H, 8.78. Found: C, 72.23; H, 8.87.

Attempted Rearrangement of 8. Reaction of chloride **8** (23.1 g, 0.125 mol) with ethylmagnesium bromide (0.125 mol) in ether (90 ml) was carried out under nitrogen at −10° just as described above for chloride **7** in tetrahydrofuran, using anhydrous cobaltous chloride (0.5 g). The reaction mixture again became hot and cooling was necessary. The reaction was completed by refluxing for 3 hr. After processsing the reaction mixture as before, the oily residue was fractionated: I, bp 28–35° (0.55 mm), 5.77 g; II, bp 35–65° (0.5–0.7 mm), 0.83 g; III, bp 60–70° (0.55 mm), 6.3 g; and a residue, 8.74 g. The nature and composition of these various fractions were established *via* glpc (20% SE-30 on Firebrick, 180°), ir, and nmr comparison with authentic materials. No glpc was done, however, on dimer **15**. Fraction I on redistillation at 750 mm afforded solvent and silane **13** (3.94 g). Fraction II consisted of unreacted chloride **8** (50%), silane **14** (29%), silane **13** (14%), and a trace (7% of the 0.83-g fraction) of chloromethyldimethylchlorosilane used to prepare **8**. Fraction III was found to be unchanged **8** and silane **14** (89 and 11%, respectively). Residual material found above eventually solidified and, after recrystallization from petroleum ether (30–60°, charcoal used), was identified as dimer **15**, mp 58.5–59.5°, mmp 57.5–58.5°, mol wt (Rast) 303 (calcd 294.5). With the composition of the fractions established, calculation then gave the product percentages listed in Table I. The mass balance was 99.2%, based upon recovery of 26% of **8**.

Control Studies. With the aid of synthetic mixtures containing the known products **13** and **14**, together with the rearranged possibilities—silanes **16** and **17**—in various concentrations, the latter two compounds were easily detectable in concentrations of above 5% *via* ir, nmr, and glpc methods. No such rearranged silanes were found in the reaction product from **8**. Also, dimer **15** as the "crude" reaction product showed no evidence of impurity spectrally. Its readiness to solidify also attests to its initial high state of purity.

Benzyldimethylsilane (**16**, 3.0 g, 20 mmol) was treated with ethylmagnesium bromide (66.7 mmol) in ether (30 ml) at −10° under nitrogen. The black mixture was then heated under reflux for 3 hr and processed as described above. Residual material weighed 2.7 g and consisted of unchanged **16** (94%) and ethylated material, silane **17** (6%).

In another experiment an equivalent amount of **16** was added to chloride **8** in a Kharasch–Grignard study exactly as detailed above. The usual products were again formed, together with recovered **16** and **17** in the ratio 14.8:1.0. Significantly, however, a somewhat higher yield of dimeric product was formed and it would not solidify. Spectral examination indicated that it was a mixture of unrearranged dimer **15** and the half-rearranged dimer **18**, each of which was easily seen in the spectra because of their considerably different absorptions. The two dimers were differentiable in mixtures by glpc, ir, and nmr. In the first, **18** had an 11-min longer retention time on SE-30 at 185° (helium flow 60 cc $\mathrm{min^{-1}}$). Absorptions at 8.3 and 8.67 μ distinguished **18** from **15** and 5% of the former could be detected in the latter. A solution of 10% of **18** in **15** (as a 33% solution in carbon tetrachloride) was readily resolvable by nmr.

Last, reaction of benzyldimethylchlorosilane with ethylmagnesium bromide as described above, but in the presence of 3% anhydrous cobaltous chloride, led to the ethylated silane **17** in 60% yield, identical in all respects with that obtained without the cobaltous chloride. No products were formed with glpc retention times equal to those from the reaction of chloride **8**, as the "reverse" silaneophyl rearrangement did not occur, a result in agreement with a different study of the same radical.[35]

Kharasch–Grignard Reaction with Silaneopentyl Chloride (9). Materials. Chloride **9** was obtained from the Pierce Chemical Co., Rockford, Ill., and was homogeneous on SE-30 at 133° and Carbowax 20 M at 119° in glpc. **Tetramethylsilane (19)** was Matheson Coleman and Bell material that showed only the δ 0.0 resonance. **2,2,5,5-Tetramethyl-2,5-disilahexane** (bisilaneopentyl, **20**) was obtained by the method of Andreev[31] [71.7%; bp 151–153° (750 mm); $n^{20}\mathrm{D}$ 1.4200; $d^{20}{}_4$ 0.747; λ^{neat} 3.38, 3.45 (CH), 8.03, 11.9, 13.38 ($\mathrm{CH_3Si}$), 7.13, 7.8, 8.84, 9.49, 13.25, 14.54 μ; $\delta^{\text{neat}}_{\text{int dioxane}}$ 0.05 ($\mathrm{CH_3Si}$), 0.5 ($\mathrm{CH_2CH_2}$); lit.[31] bp 151–153°, $n^{20}\mathrm{D}$ 1.4200, $d^{20}{}_4$ 0.7538]. **Trimethyl-*n*-propylsilane (21)** was prepared by reaction of *n*-propylmagnesium bromide and trimethylchlorosilane (Peninsular Chemical Research, Inc., Gainesville, Fla.) on a 0.3-mol scale in the usual fashion in dry ether. After processing the reaction, the ether phase contained siloxane impurities. These were removed by a wash with concentrated sulfuric acid with **21** being removed *via* a pentane wash. Distillation of the pentane solution then afforded **21** as a colorless oil [17.8%; bp 87–89° (748 mm); $n^{20}\mathrm{D}$ 1.3933; $d^{22}{}_4$ 0.690; λ^{neat} 3.45, 3.52 (CH), 8.05, 11.8 ($\mathrm{CH_3Si}$), 6.87, 7.12, 7.30, 7.52, 7.77, 8.86, 9.40, 10.02, 11.18, 13.45, 14.5 μ; $\delta^{\text{neat}}_{\text{int dioxane}}$ 1.75–0.46 m ($\mathrm{CH_3CH_2CH_2}$), 0.08 s ($\mathrm{CH_3Si}$); lit.[47] bp 90° (760 mm), $n^{20}\mathrm{D}$ 1.3929, $d^{20}{}_4$ 0.7020].

Attempted Rearrangement of 9. In a reaction apparatus equipped with two traps cooled at −70° to catch volatile products was prepared ethylmagnesium bromide (0.1 mol) in dry tetrahydrofuran (35 ml). Chloride **9** (12.27 g, 0.1 mol) was then added, followed by anhydrous cobaltous chloride (0.4 g, 3 mmol), the latter being added in one portion after the system was cooled to −6°. The mixture turned black and evolved heat and gas. After this initial reaction, the solution was refluxed for 3.25 hr, cooled, and hydrolyzed with a mixture of saturated sodium chloride solution con-

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(47) F. C. Whitmore, L. H. Sommer, P. A. DiGiorgic, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *J. Amer. Chem. Soc.*, 68, 425 (1946).

taining hydrochloric acid (pH 2). Further hydrochloric acid and tetrahydrofuran were added until two clear phases resulted. The tetrahydrofuran phase was dried and distilled, the first fraction (2.26 g) being collected in receivers at −70°. The solvent was then carefully removed through a Podbielniak Heligrid column and the residual material afterward through a 6-in. Vigreux column: II, bp 43–100° (2.35 g); III, bp 100–140° (2.77 g); IV, bp 140–155° (1.10 g); and a residue (1.98 g). Material in the cold traps from the reaction weighed 0.95 g. By nmr and glpc analysis (Carbowax 20M at 120°) these fractions were determined to contain silane **19** (1.18 g), starting chloride **9** (2.11 g), dimer **20** (1.98 g), and a trace of silane **21**, giving the yields gathered in Table I based on consumed reactant **9**. No control studies on possible rearranged products were performed. While the mass balance is not high in the reaction, no spectral evidence was found for any rearranged substance. The experimental problems associated with some of the reaction products probably occasioned the poor mass balance.

Kharasch–Grignard Reaction with Neophyl Chloride. This reaction was carried out on a 0.125-mol scale exactly as detailed by Rüchardt and Trautwein.[20h] Though the initial reaction was begun at −10°, no obvious reaction was observed until 20° was reached, a clear difference from the silicon cases. Processing the reaction mixture led to the following products: ***t*-butylbenzene**, 3.21 g (68% of the hydrocarbon fraction); **isobutylbenzene**, 0.58 g (12.4%); **2-methyl-1-phenylpropene**, 0.19 g (4.1%); and **2-methyl-3-phenylpropene**, 0.67 g (14.5%). The hydrocarbon yield was 34.5%, with a dimer mixture as residue (5.94 g). Neophyl chloride was recovered also (22.2%). Addition of the rearranged product percentages gives 31% rearrangement. Other such reactions gave as high as 33% rearrangement. Rüchardt and Trautwein[20h] report for the hydrocarbons as listed above: 66.4, 10.8, 6.2, and 16.6%, with a hydrocarbon yield of 44% and a rearrangement percentage of 33.6%. The agreement is considered very good.

Miscellaneous Reactions. Epoxyethyldimethylphenylsilane (23) was synthesized by epoxidation of phenyldimethylvinylsilane, prepared as reported,[48] with trifluoroperoxyacetic acid according to the directions of Eisch and Trainor for the triphenyl analog[45] [31.6%; bp 55.5° (0.2 mm); $n^{21}\mathrm{D}$ 1.5181; $d^{24}{}_{4}$ 0.984; λ^{neat} 3.3, 3.40, 3.44 (CH), 7.0, 8.97 (PhSi), 8.02 (CH_3Si), 8.12, 10.56, 11.37 (epoxide), 7.12, 7.61, 11.9, 14.9 μ; $\delta^{\text{neat}}_{\text{ext TMS}}$ 7.1–7.4 m (ArH), 6.8–7.0 (*o*-ArH), 1.75–2.50 m (ABC pattern, epoxide H's), −0.18 d (CH_3Si, split by the adjacent asymmetry of the epoxide ring carbon)].

Anal. Calcd for $C_{10}H_{14}OSi$: C, 67.37; H, 7.92. Found: C, 67.63; H, 8.24.

Treatment of **23** with 2,4-DNP reagent produced acetaldehyde 2,4-dinitrophenylhydrazene, confirmed by mixture melting point and spectral comparison with known material. **Phenyldimethylvinyloxysilane** was prepared by repeatedly injecting epoxide **23** into the gas chromatograph (an old SE-30 column, 5 ft × 0.25 in. copper, 187°, 60 cc min^{-1} He flow). About 16% rearrangement occurred per pass. The product was eventually collected as a colorless liquid [λ^{neat} 3.27, 3.32, 3.38, 3.41 (CH), 7.00, 8.95 (PhSi), 7.98, 12.1 (CH_3Si), 6.11, 8.52, 10.56 (vinyl ether), 7.18, 7.59, 9.82, 10.18, 12.65, 13.72, 14.35 μ; $\delta^{\text{CCl}_4}_{\text{ext TMS}}$ 7.2–7.7 m (ArH), 6.4 dd ($-CH{=}CH_2$, $J_{trans} = 13.5$ Hz, $J_{cis} = 6$ Hz), 4.45 d ($-CH{=}CH_{trans}H$), 4.1 d ($-CH{=}CH_{cis}H$), 0.4 s (CH_3Si)].

Anal. Calcd for $C_{10}H_{14}OSi$: C, 67.37; H, 7.92. Found: C, 67.33; H, 7.84.

This rearrangement did not occur on Carbowax 20M glpc columns or on new SE-30 columns. Though relatively clean, small amounts of unidentified by-products accompanied the process. The history and use of the "effective" SE-30 column is, unfortunately, lost in the sands of time.

One attempted rearrangement of **23** by the method of Eisch and Trainor[11] using magnesium bromide etherate led to diphenyltetramethyldisiloxane (**24**), identified by comparison with material obtained by the hydrolysis of phenyldimethylchlorosilane [$\delta^{\text{CCl}_4}_{\text{int TMS}}$ 7.1–7.7 m (ArH), 0.33 s (CH_3Si)].

Phenyldimethylsilylacetaldehyde diethyl acetal (25) was synthesized by reaction of silaneophylmagnesium chloride (0.2 mol) and ethyl orthoformate (29.6 g, 0.2 mol) in dry ether under reflux for 6 hr. The usual work-up afforded the acetal **25** as a colorless oil [9.0 g; 19.8%; bp 81–85° (0.75 mm); λ^{neat} 3.3, 3.4, 3.5 (CH), 7.0, 9.04 (PhSi), 8.06, 12.0–12.3 (CH_3Si), 8.42, 9.1, 9.55, 10.1 (CO) μ; $\delta^{\text{neat}}_{\text{int TMS}}$ 6.8–7.3 m (ArH), 4.28 t ($-CH<$), 2.7–3.5 m (nonequivalent CH_2 of OEt, ABX_3), 0.7–1.0 q (CH_3 of OEt, also $SiCH_2$ d superimposed), −0.03 s (CH_3Si)].

All attempts to hydrolyze **25** to aldehyde **5** led instead to acetaldehyde (identified by its 2,4-DNP derivative) and siloxane **24**.

Phenyldimethylsilylacetic acid was made as reported (55%, mp 85.5–86.5°, lit.[49] mp 90°). Its treatment with thionyl chloride on a steam bath for 2.5 hr gave no acid chloride, but rather phenyldimethylchlorosilane (75%, bp 38–40° (0.25 mm)), identical in all respects with commercial material (Pierce Chemical Co.).

Epoxyethyltrimethylsilane (26) was obtained as described[50] [44.5%; bp 106–110° (751 mm); $n^{23.5}\mathrm{D}$ 1.4140; λ^{neat} 3.32, 3.42 (CH), 8.05, 11.95, 13.33 (CH_3Si), 8.15, 9.58, 11.35 (epoxide) μ; $\delta^{\text{neat}}_{\text{ext TMS}}$ 1.8–2.65 m (epoxide H's, ABX pattern, $J_{gem} = 6.5$ Hz, $J_{cis} = 5.3$ Hz, $J_{trans} = 4.3$ Hz), −0.23 s (CH_3Si); lit.[50] bp 107° (atm), $n^{19}\mathrm{D}$ 1.4144]. Treatment of **26** with 2,4-DNP reagent again gave acetaldehyde 2,4-DNP.

2-Trimethylsilylethanol (27) was synthesized by the method of Speier and coworkers[51] [75%; bp 67–75° (57 mm); λ^{neat} 3.05 (OH), 3.41, 3.50 (CH), 8.03, 12.0, 13.15 (CH_3Si), 9.65 (CO) μ; $\delta^{\text{neat}}_{\text{ext TSM}}$ 4.68 s (OH), 3.43 t (CH_2OH), 0.67 t ($SiCH_2$), −0.17 s (CH_3Si); lit.[51] bp 95° (100 mm)].

Various attempts to oxidize **27** to aldehyde **6** that failed included: lead tetraacetate in pyridine, chromium trioxide in pyridine, and sodium dichromate and sulfuric acid in ether and ethyl azodicarboxylate. An exploratory attempt to effect oxidation *via* its tosylate in dimethyl sulfoxide and base failed also.

β-Phenethyldimethylphenylsilane was an interesting product from the attempted formation of bisilaneophyl (**15**) by the Wurtz reaction, *i.e.*, treatment of silaneophyl chloride (**8**, 9.25 g, 0.05 mol) with sodium (2.3 g, 0.1 g-atom) in refluxing dry toluene (50 ml) under nitrogen for 11 hr. The solution was filtered and the toluene was removed. Distillation then gave mostly trimethylphenylsilane (**13**), but a fraction was also obtained beyond this [1.8 g, 15%, bp 125–130°] that by spectral evidence possessed the structure of β-phenethyldimethylphenylsilane. The analytical sample was collected from an SE-30 glpc column at 198°; $n^{20}\mathrm{D}$ 1.550; $d^{24}{}_{4}$ 0.953; λ^{neat} 3.31, 3.48 (CH), 7.03, 9.01 (PhSi), 8.04, 12.0 (CH_3Si), 6.70, 6.90, 8.6, 11.15, 12.38, 13.0, 13.75, 14.35 μ; $\delta^{\text{CCl}_4}_{\text{int dioxane}}$ 7.38–7.85 m (PhSi H's), 7.31 s ($C_6H_5CH_2$), 2.65–3.00 m ($PhCH_2CH_2Si$), 1.15–1.50 m ($PhCH_2CH_2Si$, these methylenes are complex A_2B_2 or AA′BB′ patterns), 0.43 s (CH_3Si)].

Anal. Calcd for $C_{16}H_{20}Si$: C, 79.94; H, 8.39. Found: C, 79.97; H, 8.14.

The formation of this compound probably arises from reaction of silaneophylsodium with toluene to form benzylsodium and silane **13** followed by a displacement reaction by benzylsodium upon chloride **8**. Similar reactions have been observed by others.[28]

Diphenylchloromethylsilanol resulted from an attempted synthesis of chloride **7** in ether as detailed by Huang and Wong.[13] The solid product so obtained was fractionally crystallized to give some **7** but also the above silanol [26%; mp 54–55°; λ^{Nujol} 3.15 (OH), 7.02, 9.0 (PhSi), 6.3, 6.75, 8.91, 9.35–9.8, 10.03, 11.85, 12.88, 13.15, 13.6, 14.35 μ; $\delta^{\text{CCl}_4}_{\text{int dioxane}}$ 7.5–8.0 m (ArH), 4.6 s (OH), 3.33 s (CH_2Cl), soluble in 10% aqueous sodium hydroxide, regenerated upon acidification].

Anal. Calcd for $C_{13}H_{13}OClSi$: C, 62.77; H, 5.27. Found: C, 63.17; H, 5.29.

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