Aryl Shifts from Silicon to Carbon via γ- and δ-Silyl Radicals[1,2]

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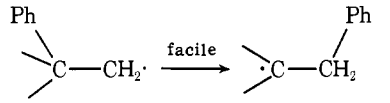
Abstract: A series of 12 γ- and δ-halosilanes was prepared and characterized. Reduction of these halides at 140 °C with di-*tert*-butyl peroxide as the initiator led to the formation of rearranged as well as unrearranged products, all of which were separately synthesized for authentic comparison. The rearranged products arose from 1,4- or 1,5-aryl shifts from silicon to carbon and are the first such rearrangements to be reported. These shifts proceed via Ar_1-5 or Ar_1-6 spiro radical transition states and/or intermediates. Aryl substituents increased the rearrangement somewhat. Chlorosilanes gave more rearranged product than did bromosilanes. This was due to removal of rearranged product by its subsequent reaction with starting material in the case of the bromosilanes. The mechanistic pathway for these processes is discussed.

Introduction

The striking contrast in behavior toward rearrangement between neophyl and related radicals and their silicon congeners can be exemplified by a number of well-established free radical reactions: peroxide-induced decarbonylation of aldehydes, the Kharasch–Grignard reaction of halides, and the reduction of halides with organotin hydrides.[3] In all cases thus far examined, the 1,2 shift of phenyl from carbon to carbon is relatively facile whereas the analogous shift of phenyl from silicon to carbon remains unobserved (eq 1, 2).



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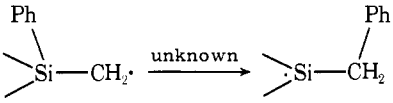

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Of the suggested[4] anti-rearrangement factors that might be responsible for this behavior of α-silyl radicals, two can be tested in tandem, viz., stabilization of α-silyl radicals by dπ–pπ electron delocalization ("back-bonding") and the steric strain associated with an Ar_1-3 transition state. Removal of the radical site from the α to a more distant position would preclude both the possibility of back-bonding and the necessity for an Ar_1-3 transition state. If rearrangement could be found for such a more distant radical, then the absence of rearrangement in the α case might be more securely blamed on the above factors. For this reason the present study of aryl migration in γ- and δ-silyl radicals was undertaken.

Results

A series of 12 γ- and δ-halosilanes was prepared as shown in Schemes I and II. These syntheses were straightforward (see Experimental Section) and warrant only brief additional comment. The hydroboration–oxidation[5] of **2**-H to **3**-H produced a small amount (7%) of secondary alcohol as well. The contaminant (as its bromide) was removed from bromide **4**-H by gas chromatography. Because this possibility for contamination existed, all the bromides were so purified. Method I-C[6] applied to **2**-OCH_3 led to *p*-bromoanisole instead of **4**-OCH_3. Presumably the highly activated *p*-anisyl ring allowed a facile bromodesilylation reaction[7] in this case. Attempted homolytic addition of hydrogen bromide to **2**-X was unsatisfactory. Although some **4**-X was produced, significant quantities of secondary bromides also resulted. Selected properties of the halosilanes and their precursors are given in Table III (see Experimental Section).

Scheme I

I-A $p\text{-}XC_6H_4MgBr + Cl_3SiCH_2CH_2CH_2Cl$

X = H, OCH_3, CH_3, F

$\xrightarrow{\text{ether}}$ $[p\text{-}XC_6H_4SiCl_2CH_2CH_2CH_2Cl]$

$\xrightarrow[\text{ether}]{2CH_3MgI}$ $p\text{-}XC_6H_4Si(CH_3)_2CH_2CH_2CH_2Cl$ **1-X**

I-B $p\text{-}XC_6H_4MgBr + (CH_3)_2SiCl_2$

$\xrightarrow{\text{ether}}$ $p\text{-}XC_6H_4Si(CH_3)_2Cl$

$\xrightarrow[\text{ether}]{CH_2{=}CHCH_2MgCl}$ $p\text{-}XC_6H_4Si(CH_3)_2CH_2CH{=}CH_2$ **2-X**

$\xrightarrow[2.\ NaOH,\ H_2O_2]{1.\ B_2H_6,\ THF}$ $p\text{-}XC_6H_4Si(CH_3)_2CH_2CH_2CH_2OH$ **3-X** (X = H, OCH_3)

$\xrightarrow[2.\ LiBr,\ acetone]{1.\ TsCl,\ py}$ $p\text{-}XC_6H_4Si(CH_3)_2CH_2CH_2CH_2Br$ **4-X** (X = H, OCH_3)

I-C **2-X** $\xrightarrow[2.\ Br_2,\ NaOCH_3]{1.\ B_2H_6,\ THF}$ **4-X** (X = CH_3, F)

Scheme II

$p\text{-}YC_6H_4Si(CH_3)_2CH_2CH_2CH_2CH_2Cl$ **5-Y**

$CH_2{=}CHCH_2CH_2Cl,\ H_2PtCl_6$

II-A $p\text{-}YC_6H_4Si(CH_3)_2Cl \xrightarrow[LiAlH_4]{} p\text{-}YC_6H_4Si(CH_3)_2H$

Y = H, CH_3

$CH_2{=}CHCH_2CH_2Br,\ H_2PtCl_6$

$p\text{-}YC_6H_4Si(CH_3)_2CH_2CH_2CH_2CH_2Br$ **6-Y**

II-B $p\text{-}CH_3C_6H_4Si(CH_3)_2Cl + HO(CH_2)_4Cl$

$\longrightarrow p\text{-}CH_3C_6H_4Si(CH_3)_2O(CH_2)_4Cl$

$\xrightarrow[3.\ HCl]{1.\ Mg,\ ether\ \ 2.\ \Delta}$ $p\text{-}CH_3C_6H_4Si(CH_3)_2CH_2CH_2CH_2CH_2OH$

$\xrightarrow[2.\ LiBr,\ acetone]{1.\ TsCl,\ py}$ **6-**CH_3

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Table I. Reductive Rearrangement of Halosilanes (Benzene Solvent, 140 ± 5 °C, 20 h)

run	reactant	% rearrangement, initial concn of halosilane, M[a] 10^{-1}	10^{-2}	10^{-3}	rearranged product
		γ-Chlorosilanes			
1	**1**-H	4.5	15.	*b*	**9**-H
2	**1**-OCH_3	12.	26.	41.	**9**-OCH_3
3	**1**-CH_3	5.5	19.	31.	**9**-*p*-CH_3[c]
4	**1**-F	5.0	16.	28. (25.)[d]	**9**-F[e]
		γ-Bromosilanes			
5	**4**-H	tr	4.0	28.	**9**-H
6	**4**-OCH_3[f]				
7	**4**-CH_3	2.3	6.1	30.	**9**-p-CH_3
8	**4**-F	2.0	4.8	21. (9.0)[d]	**9**-F
		δ-Chlorosilanes			
9	**5**-H	2.5	21.	*b*	**10**-H
10	**5**-CH_3	7.0	25.	33.	**10**-CH_3
		δ-Bromosilanes			
11	**6**-H	tr	1.5	16.	**10**-H
12	**6**-CH_3	tr	3.0	27.	**10**-CH_3
		Miscellaneous			
13	**1**-F, **4**-F	*b*	*b*	(13.)[d]	**9**-F

[a] Molar ratios were halosilanes:tri-*n*-butyltin hydride:di-*tert*-butyl peroxide = 10:3.3:1. Only a trace of rearranged product (<0.1%) was detected at 1 M concentration for the chlorosilanes and none for the bromosilanes. The rearrangement percentages are for duplicate runs and are ±3%. The values have been given to two significant figures. [b] Not investigated. [c] Differentiable from **9**-*m*-CH_3 by gas chromatography. [d] The initial halosilane concentration was 5×10^{-3} M. [e] Both **9**-F and **9**-OCH_3 showed clear para aromatic NMR patterns. [f] This bromide was a sensitive substance that underwent change thermally and (seemingly) independently of the homolytic process under study. It is included for completeness, although only unrearranged product (35–38%) and several unidentified other substances were obtained.

Scheme III

III-A p-$XC_6H_4MgBr + (CH_3)_2SiCl_2$

$\xrightarrow{\text{ether}}$ p-$XC_6H_4Si(CH_3)_2Cl$

$\xrightarrow{n\text{-}C_4H_9MgBr}$ p-$XC_6H_4Si(CH_3)_2CH_2CH_2CH_2CH_3$ (**8**-X (X = H, CH_3))

$\xrightarrow{n\text{-}C_3H_7MgBr}$ p-$XC_6H_4Si(CH_3)_2CH_2CH_2CH_3$ (**7**-X (X = H, OCH_3, CH_3, F))

III-B $XC_6H_4(CH_2)_mMgBr + (CH_3)_2SiCl_2$

$\xrightarrow{\text{ether}}$ $XC_6H_4(CH_2)_mSi(CH_3)_2Cl$

$\xrightarrow{LiAlH_4}$ $XC_6H_4(CH_2)_mSiH(CH_3)_2$

9-X (m = 3; p-X = H, OCH_3, CH_3, F; m-X = CH_3)

10-X (m = 4; p-X = CH_3)

Over a 20-h period, the halosilanes were reduced with tri-*n*-butyltin hydride (TBTH)[8] in benzene with di-*tert*-butyl peroxide (DTBP) as initiator. The molar ratios of the reactants were held constant but the concentrations were varied. The reaction temperature was 140 ± 5 °C. The reductions were quite clean and afforded both unrearranged and rearranged products in proportions dependent upon the concentrations involved. The results of the reduction studies are given in Table I.

To confirm the structures of the reduced products, alternative syntheses were achieved as shown in Scheme III according to well-established procedures. Some properties of these silanes are also included in Table III (see Experimental Section).

The results of the present studies given in Table I may be summarized as follows: (a) these rearrangements are not particularly facile, occurring significantly only in dilute solution; (b) rearrangement increases with dilution for both chlorides and bromides (e.g., runs 4 and 8); (c) chlorides seemingly afford more rearranged product than do bromides, but the difference decreases with increased dilution (e.g., runs 3 vs. 7 and 10 vs. 12); (d) the extent of rearrangement increases slightly with substituted aryl groups (runs 1–4); and (e) the rearrangement produces para-substituted products from para-substituted reactants and is therefore an Ar_1 process (e.g., runs 2 and 3).

The increased rearrangement observed with the chlorides relative to the bromides is noteworthy and unexpected. Normally, intermediates react independently of their source. But the reduction of a mixture of **1**-F and **4**-F (run 13, Table I) gave rearranged **9**-F in a percentage that indicated that both halosilanes were of comparable reactivity (within threefold). This is a marked contrast to the normally enormous (ca. 10^4-fold) greater reactivity of bromides vs. chlorides.[9] This led to a suggestion that the halosilanes differed in the nature of the initial radical each formed in this process.[1b] Interest by others in this unusual difference between the halosilanes led to further study.[10] Competitive reduction of equimolar **1**-F and **4**-F with limited TBTH at 140 °C for 12 h showed that **4**-F was totally reduced whereas **1**-F was not significantly affected. So the halosilanes do differ greatly in reactivity, and our earlier view[1b] must be changed. Further competitive reductions demonstrated that **4**-F was comparable in reactivity to an all-carbon bromide, γ-phenylpropyl bromide, and that **1**-F was likewise comparable in reactivity to *n*-heptyl chloride. Thus, no special reactivity or lack thereof resides in these halosilanes, and the disparity between them in rearranged product formation must arise in some other way. Because the bromosilanes were so readily reduced compared to the chlorosilanes, two further tests were conducted. In the first, separate reactions of **1**-F and **4**-F with TBTH and DTBP were conducted such that a mixture of hydride and peroxide was added by syringe to the hot (165 °C) halosilanes in diphenyl ether. In this way, any reduction of the more reactive **4**-F at lower temperatures during warmup (where rearrangement would be expected to be less facile) could be avoided. If this be the cause for lowered rearrangement from the bromosilanes, such a change in reaction procedure should equalize the results from either halosilane. However, **1**-F still showed more rearranged product than did **4**-F. The last test reaction again involved separate treatment of **1**-F and **4**-F with **9**-F over a 14-h period at 140 °C in the presence of DTBP (eq 3). Whereas **1**-F was not affected under these conditions, **4**-F was partially reduced to **7**-F. Clearly, therefore, the source of the lowered rearrangement from the bromosilanes is the removal of rearranged silane by its further reaction with starting material.[11]

(1-F) p-$FC_6H_4Si(CH_3)_2CH_2CH_2CH_2Cl$

$\xrightarrow[\text{DTBP, }\Delta]{\text{>SiH (9-F)}}$ no reaction (3)

(4-F) p-$FC_6H_4Si(CH_3)_2CH_2CH_2CH_2Br$

$\xrightarrow[\text{DTBP, }\Delta]{\text{>SiH (9-F)}}$ p-$FC_6H_4Si(CH_3)_2CH_2CH_2CH_3$ (**7**-F)

Discussion

The reduction of these halosilanes undoubtedly follows the accepted free-radical pathway ascribed to such reactions,[8] as modified for potential reversible[12] rearrangement. The pathway is shown in Scheme IV for chlorides **1** and **5**.

Scheme IV

$$(t\text{-BuO})_2 \xrightarrow[\Delta]{} 2 \cdot \text{O-}t\text{-Bu}$$

$$n\text{-Bu}_3\text{SnH} + \cdot \text{O-}t\text{-Bu} \longrightarrow \cdot \text{Sn}(n\text{-Bu})_3 + \text{HO-}t\text{-Bu}$$

$$\mathbf{1}\ (\mathbf{5}) + \cdot \text{Sn}(n\text{-Bu})_3 \xrightarrow{k_{hal}} \mathbf{1} \cdot (\mathbf{5} \cdot) + \text{Hal-Sn}(n\text{-Bu})_3$$

$$\mathbf{1} \cdot (\mathbf{5} \cdot) \underset{k'_r}{\overset{k_r}{\rightleftarrows}} \mathbf{9} \cdot (\mathbf{10} \cdot)$$

$$\mathbf{1} \cdot (\mathbf{5} \cdot) + \text{H-Sn}(n\text{-Bu})_3 \xrightarrow{k_H} \mathbf{7}\ (\mathbf{8})$$

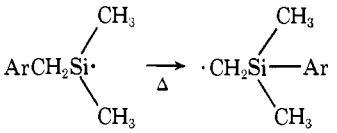
$$\mathbf{9} \cdot (\mathbf{10} \cdot) + \text{H-Sn}(n\text{-Bu})_3 \xrightarrow{k_H} \mathbf{9}\ (\mathbf{10})$$

The formation of ***9*** *and* ***10*** *represents the first reported 1,4 and 1,5 migration of an aryl group from silicon to carbon.*[13] Clearly no prohibition against these migrations exists, in contrast to the unknown 1,2 shifts. The inference may be drawn that α-silyl radical stability and/or transition state steric strain may therefore be the principal anti-rearrangement factors blocking the 1,2 shift. That α-silyl radical stability may be the *critical* anti-rearrangement factor is indicated by two further points. Aralkyldimethylsilanes rearrange thermally to aryltrimethylsilanes (eq 4),[14] a transformation explicable as a conversion of a silyl radical into a more stable α-silyl radical (eq 5).

$$\text{G-C}_6\text{H}_4\text{CH}_2\text{SiH(CH}_3)_2 \xrightarrow{440\ ^\circ\text{C}} \text{CH}_3\text{Si(CH}_3)_2\text{C}_6\text{H}_4\text{-G} \quad (4)$$

(G = H, *p*-CH_3, *m*-CH_3) (site retention by G)

Presumably the Ar_1-3 transition state strain presents no insurmountable barrier to this 1,2 shift, which is the *reverse* of the unknown case (eq 2). Because the same Ar_1-3 transition



(5)

state would be involved in either direction of rearrangement, this factor cannot be critical. Rather, the process simply reflects the relative energies of the radicals involved (Figure 1). As a second indication that α-silyl radical stability is the cause for nonrearrangement, one may cite the fact that α-chlorosilanes (even aliphatic examples) are more reactive toward tri-*n*-butyltin hydride than their α-chloroalkane analogues in competition studies (an example is given in eq 6).[15] This increased reactivity of α-chlorosilanes, particularly the example in eq 6, again demonstrates the stability of α-silyl radicals.

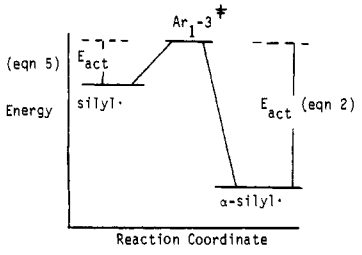


Figure 1. Relative energetics of 1,2 aryl shifts to and from silicon radical species.

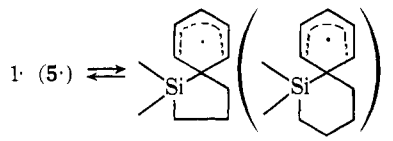
$$\text{ClCH}_2\text{Si(CH}_3)_2\text{CH}_2\text{CH}_2\text{C(CH}_3)_2\text{CH}_2\text{Cl} \xrightarrow[\text{AIBN, 366 nm}]{n\text{-Bu}_3\text{SnH (1 mol)}} \text{CH}_3\text{Si(CH}_3)_2\text{CH}_2\text{CH}_2\text{C(CH}_3)_2\text{CH}_2\text{Cl} \quad (6)$$

Scheme IV readily explains the increased rearrangement with increased dilution. Because organotin hydrides are excellent hydrogen donors, dilute solutions are needed before the lifetime of **1** · (**5** ·) is sufficient to allow rearrangement. In a formal sense, the extent of rearrangement is proportional to $[\text{HSn}(n\text{-Bu})_3]^{-1}$, assuming that k_H does not vary for any species. This proportionality cannot be utilized exactly in the present study, however, because the tin hydride concentration decreases with time.[16] Conceptually, however, lowered concentrations of the tin hydride should increase the lifetime of **1** · (**5** ·) and raise the rearrangement percentage as found.

The exact relationship used by others[17] to relate the concentration of rearranged product (RH) and the initial concentration of TBTH (S_0), which is totally consumed, is shown in eq 7, where $r = k_r/k_H$ of Scheme IV.

$$[\text{RH}] = r \ln\left[\frac{S_0 + r}{r}\right] \quad (7)$$

Use of an iterative computer program to calculate *r* values led to highly variable results, examples of which for **1**-F were $r = 3.6 \times 10^{-4}$, 1.8×10^{-4}, and 4.3×10^{-5} for $[S_0] = 3.3 \times 10^{-2}$, 3.3×10^{-3} and 3.3×10^{-4} M, respectively. The *r* values for the bromosilane cases were discarded as meaningless because the rearrangement percentages do not reflect the true values owing to subsequent reaction (vide supra). The variation in *r* indicates that eq 7 is improper for the present system, although the order of magnitude of *r* (ca. 10^{-4}) does rationalize the relatively nonfacile nature of these 1,4- and 1,5-aryl shifts. The impropriety in eq 7 lies in the assumption of irreversibility in the rearrangement step k_r. The *reversibility of this step must be included in the proper treatment.* The retention of para orientation in the products indicates that this rearrangement step proceeds via an Ar_1-5 (or Ar_1-6) pathway, as shown in eq 8. At low concentrations of reactants, the system would approach equilibrium and the product composition from the halosilanes would become similar (e.g., runs 3 and 7 in Table II). At any concentration of reactants higher than that which



(8)

allows such equilibration, subsequent removal of **9** (**10**) by further reaction (eq 3) would afford different product compositions from the halosilanes, as found. By including step k'_r

Table II. Calculated Competition, Equilibrium, and Rearrangement Data[a]

			% rearrangement (obsd)[b] at $[S_0]$		
1-X	$10^4 r$, mol/L	K_e	3.3×10^{-2} M	3.3×10^{-3} M	3.3×10^{-4} M
1-H	5.4	0.33 (K_0)	4.6 (4.5)	15 (15)	*c*
1-F	4.5	0.45	4.3 (5)	16 (16)	28 (28)
1-CH_3	6.1	0.50	5.4 (5.5)	19 (19)	31 (31)
1-OCH_3	14.	0.67	10 (12)	28 (26)	38 (41)

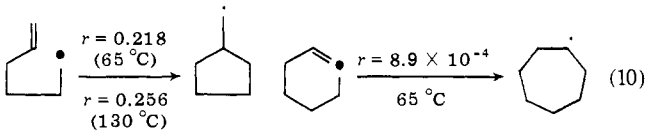
[a] Calculated by iterative computer program using eq 9. [b] From Table I. [c] Not determined.

in the derivation procedure used to obtain eq 7, the following revised relation may be derived:[20]

$$[RH] = r \ln \left[\frac{S_0 + r(1+\theta)}{r(1+\theta)} \right] \quad (9)$$

where $r = k_r/k_H$ (as in eq 7) and $\theta = k'_r/k_r = 1/K_e$, i.e., the recriprocal of the equilibrium constant relating **1** · and **9** · (**5** · and **10** ·) An iterative computer program was then again used to calculate appropriate values for r, K_e, and rearrangement percentages (within 3%) for some chlorosilanes (Table II), using the data from Table I.[21] The acceptable agreement between calculated and observed rearrangement percentages argues effectively for the correctness of Scheme IV.

The r values for radicals **1** · may be contrasted with those shown for the 5-hexenyl (more favorable)[19,22] and 6-heptenyl (comparable)[22] radicals studied under similar reaction conditions (eq 10). Hence the rearrangement of γ- (and presumably δ-) silyl radicals via an aryl shift is not very favorable and therefore is observable indeed only under dilute conditions in the presence of TBTH.[23] In fact, the *reverse* process noted by Sakurai[12] is the more favorable direction of the equilibrium process.



(10)

The increased rearrangement observed with the substituted aryl cases (Tables I and II) is slight and its origin would be mechanistically speculative at present. Nonetheless, the trend ($\log K/K_0$) does correlate modestly with σ_p^+ values ($\rho \sim -0.5$) and a small polar effect seems apparent. Further study of other substituents must be performed to clarify this point.

Experimental Section

General. Boiling points are not corrected. Instrumental procedures used the following: Varian A-90-P gas chromatograph, Beckman IR-5A infrared spectrophotometer, Varian A-60A NMR spectrometer. Only significant spectral absorptions are given below or in Table III. All analytical samples were collected by GLC from 3% SE-30, 20% Reoplex (polypropylene glycol adipate), or 10% FFAP columns at 150–180 °C using helium carrier gas. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. General descriptions of the synthetic methods listed in Schemes I, II, and III are given below. Individual preparations differed insignificantly from these general directions.

γ-Chlorosilanes, 1 (Procedure I-A). The appropriate arylmagnesium bromide (0.1 mol) in ether (40 mL) was added dropwise at 25 °C with stirring to a solution of 3-chloropropyltrichlorosilane (PCR, Inc., Gainesville, Fla., 21.2 g, 0.1 mol) in ether (75 mL) in a system protected from moisture. After 1 h the solution was refluxed for an additional time period (1.5–5 h). Methylmagnesium iodide (0.21 mol) in ether (50 mL) was then added dropwise to the cooled solution and the resulting mixture was refluxed for 15–28 h, with additional ether being added occasionally to maintain fluidity. Hydrolysis was accomplished at 0 °C by the dropwise addition of saturated ammonium chloride solution. The ether phase was separated and washed with saturated sodium bisulfite solution (3 × 25 mL) and brine (2 × 25 mL), and then dried over sodium sulfate. Removal of the ether left a colored oil which was passed through a column of alumina (100 g) with hexane. After evaporation of the hexane the residue was distilled. See Table III. The yields follow: **1**-H (45.5%); **1**-OCH_3 (31%); **1**-CH_3 (50%); and **1**-F (34%). The n_D (°C) values follow: **1**-H, 1.515 (20); **1**-OCH_3, 1.521 (23); **1**-CH_3, 1.514 (23); and **1**-F, 1.500 (23).

Allylsilanes, 2 (Procedure I-B). Phenyldimethylchlorosilane was purchased from PCR, Inc., and **2**-H was prepared from it as reported.[24] The other aryldimethylchlorosilanes were prepared according to literature procedures: Ar = *p*-anisyl,[25] *p*-tolyl,[26] and *p*-fluorophenyl.[27] To a solution of the appropriate aryldimethylchlorosilane (0.1 mol) in ether (100 mL) was added an equivalent amount of allylmagnesium chloride (1.3 M in ether, PCR, Inc.) over a 20-min period. The milky solution was then refluxed with stirring for 20 h, with additional ether being added as needed. The reaction was processed as in procedure I-A except that sodium bicarbonate replaced sodium bisulfite and no treatment with alumina was needed. See Table III. The yields follow: **2**-H (78.5%); **2**-OCH_3 (78%); **2**-CH_3 (58%); and **2**-F (72%).

γ-Silylpropyl alcohols, 3. Alcohols **3**-H (49.5% yield) and **3**-OCH_3 (86% yield) were prepared in the usual fashion[5] from the appropriate allylsilane and diborane in tetrahydrofuran. See Table III.

γ-Bromosilanes, 4 (via Tosylates). The tosylates of the above alcohols were prepared using *p*-toluenesulfonyl chloride in pyridine. In each case, the crude tosylate (oil, 0.06 mol) was treated with lithium bromide (5.21 g, 0.06 mol), either at 90 °C in dry diglyme (25 mL) overnight for **4**-H, or at reflux for 20 h in acetone (100 mL) for **4**-OCH_3. Ether (30 mL) and water (10 mL) were added to the reaction mixture (in the case of **4**-OCH_3 after the acetone had been evaporated). The ether phase was separated and combined with ether washes (3 × 25 mL) of the aqueous layer, washed with water (6 × 25 mL), sodium bicarbonate solution (5%, 1 × 25 mL), and brine, and then dried ($MgSO_4$). Upon removal of the ether the residual oil was distilled to afford **4**-H [73%, n_D (31 °C) 1.5273, d_4 1.180 (28 °C)] or **4**-OCH_3 [66%, n_D 1.533 (23 °C)]. In the former, GLC analysis (Reoplex, 150 °C) indicated ca. 7% of another bromide, presumably the secondary bromide resulting from the minor alcohol formed in the hydroboration–oxidation of **2**-H. Although no comparable impurities were observed in other cases, all of the bromosilanes used in the reduction studies were purified by GLC before use.

γ-Bromosilanes, 4 (via Hydroboration–Bromination, Procedure I-C). Either **2**-CH_3 or **2**-F (0.05 mol) in tetrahydrofuran (50 mL) was hydroborated at 0 °C with diborane in tetrahydrofuran (1 M, Aldrich) in the normal fashion. Methanol (1.5 mL) was added afterward to destroy any excess diborane. Bromine (0.1 mol) was next added slowly so that the reaction temperature remained at 0 °C. A solution of sodium methoxide in methanol (4.16 M, 30 mL) was added dropwise at a rate to keep the temperature below 5 °C, after which the material was allowed to warm to room temperature. The solution was treated with pentane (25 mL), water (10 mL), and saturated aqueous potassium carbonate (10 mL). The pentane layer was separated and combined with pentane washes (3 × 50 mL) of the aqueous material. The organic extracts were washed with water and brine and then dried (K_2CO_3). After removal of the solvent, the remaining oil was distilled to produce **4**-CH_3 (36%) and **4**-F (54%). Application of this method to **2**-OCH_3 yielded *p*-bromoanisole.

δ-Halosilanes, 5 and 6 (Procedure II-A). The appropriate aryldimethylchlorosilane (see procedure I-B) was reduced to the silicon hydride with lithium aluminum hydride as reported: Ar = Ph,[28] Ar = *p*-tolyl.[29] The silicon hydride (0.1 mol) was added dropwise at 25 °C to a solution of either 4-chloro-[30] or 4-bromo-1-butene[30] (0.1 mol) containing chloroplatinic acid (0.12 M in ethanol, 15 drops). The addition was exothermic and must be controlled by a slow addition of the silicon hydride. After the addition, the colored mixture was stirred for an additional 1 h, then heated to 70–80 °C for 8 h. Ether was added to the cooled solution, which was filtered, washed successively with water, sodium bicarbonate solution and brine, and dried ($MgSO_4$). Upon removal of the ether, distillation produced **5**-H (50%), **5**-CH_3 (62%), **6**-H (68%), and **6**-CH_3 (60%). See Table III.

δ-Bromobutyl-*p*-tolyldimethylsilane, 6-CH_3 (Procedure II-B). As a check on the above synthetic method, the following alternative preparation of **6**-CH_3 was carried out. Tetramethylene chlorohydrin[31] (5.43 g, 0.05 mol) was mixed with *p*-tolyldimethylchlorosilane[26] (9.2 g, 0.05 mol) in dry benzene (50 mL). The solution was stirred in an ice bath as anhydrous ammonia was passed through it at a rapid rate. When the odor of ammonia persisted above the solution the mixture was filtered and distilled. δ-Chloro-*n*-butoxy-*p*-tolyldimethylsilane was obtained as a colorless oil (9.0 g, 70%, bp 116–117 °C at 0.5 mm, n_D (23 °C) 1.470). The analytical sample was collected in a Hickman still.

Anal. Calcd for $C_{13}H_{21}ClOSi$: C, 60.79; H, 8.34. Found: C, 60.66; H, 8.29.

A solution of the above ether (5.13 g, 0.02 mol) was converted to its Grignard reagent with magnesium (0.48 g, 0.02 g-atom) in ether (75 mL). When the reaction appeared to be complete, the ether was distilled off and the residue was heated at 120–125 °C for 12 h.[32] Ether (50 mL) and hydrochloric acid (diluted 1:1, 10 mL) were added. The ether layer was separated and combined with two ether washes

Table III. Selected Properties of Silanes

compd	bp, °C (mm)	^{1}H NMR, δ[a] $CH_2Cl(Br)$	$SiCH_2CH_2$	$SiCH_3$	other	anal. calcd C	anal. calcd H	anal. found C	anal. found H
				γ-Chlorosilanes					
1-H	130–135 (5.0)	3.28 t	0.5–1.92 m	0.21 s		62.08	8.05	62.06	7.89
1-OCH_3	116–118 (0.05)	3.55 t	0.6–2.2 m	0.21 s	3.9 s (OCH_3)	59.36	7.89	59.22	8.04
1-CH_3	92–93 (0.5)	3.42 t	0.6–2.0 m	0.23 s	2.36 s ($ArCH_3$)	63.54	8.44	63.40	8.63
1-F	89–92 (0.2)	3.55 t	0.6–2.1 m	0.30 s		57.25	6.99	57.25	6.99
				Allylsilanes					
2-H[b]	90–91 (4.0)	1.78 d[c]		0.26 s	4.78, 5.21, 5.51–6.26 (vinyl)				
2-OCH_3	80–85 (0.25)	1.70 d[c]		0.21 s	4.7, 5.1, 5.5–6.3 (vinyl); 3.85 s (OCH_3)	69.84	8.79	70.06	8.97
2-CH_3	59–60 (0.2)	1.75 d[c]		0.23 s	4.7, 5.2, 5.5–6.2 (vinyl); 2.4 s ($ArCH_3$)	75.71	9.53	75.62	9.66
2-F	56–57 (1.0)	1.75 d[c]		0.26 s	4.7, 5.2, 5.5–6.3 (vinyl)	67.99	7.78	67.76	8.06
				γ-Silylpropyl Alcohols					
3-H	98–99 (0.2)	3.44 t[d]	0.5–1.8 m	0.25 s	2.90 s (OH)	67.98	9.34	67.93	9.74
3-OCH_3	115–125 (0.05)	3.52 t[d]	0.4–1.8 m	0.23 s	2.2 s (OH), 3.86 s (OCH_3)	64.24	8.98	64.01	9.16
				γ-Bromosilanes					
4-H	123–126 (3.5)	3.28 t	0.7–2.1 m	0.28 s		51.35	6.66	51.35	6.40
4-OCH_3	110–113 (0.1)	3.38 t	0.6–2.2 m	0.23 s	3.86 s (OCH_3)	50.17	6.67	49.87	6.69
4-CH_3	108–110 (0.1)	3.40 t	0.6–2.2 m	0.26 s	2.4 s ($ArCH_3$)	53.13	7.06	52.93	7.20
4-F	75–76 (0.1)	3.40 t	0.6–2.2 m	0.26 s		48.00	5.86	48.01	5.79
				δ-Chlorosilanes					
5-H	79–80 (0.1)	3.37 t	0.5–1.9 m	0.25 s		63.54	8.44	63.72	8.30
5-CH_3	85–86 (0.2)	3.50 t	0.4–2.1 m	0.23 s	2.37 s ($ArCH_3$)	64.83	8.79	64.66	8.90
				δ-Bromosilanes					
6-H	123–125 (2.75)	3.28 t	0.52–2.1 m	0.25		53.13	7.06	53.04	6.94
6-CH_3	122–123 (1.5)	3.35 t	0.5–2.1 m	0.23 s	2.37 s ($ArCH_3$)	54.73	7.42	54.45	7.53
				n-Propylsilanes					
7-H[b]	82–85 (4.5)		0.65–1.5 m[e]	0.24 s					
7-OCH_3	80–85 (0.2)		0.3–1.6 m[e]	0.20 s	3.89 s (OCH_3)	69.17	9.67	68.84	9.99
7-CH_3	65–67 (0.5)		0.4–1.7 m[e]	0.20 s	2.37 s($ArCH_3$)	74.92	10.48	74.95	10.70
7-F	38–39 (0.7)		0.6–1.5 m[e]	0.23 s		67.29	8.73	67.50	8.82
				n-Butylsilanes					
8-H	92–94 (4.5)		0.53–1.5 m[e]	0.21 s		74.92	10.48	74.68	10.28
8-CH_3	68–72 (0.3)		0.4–1.6 m[e]	0.20 s	2.40 s ($ArCH_3$)	75.65	10.74	75.97	10.98
				Silicon Hydrides					
9-H[b]	78–80 (2.5)		0.38–2.6 m[f]	0.01 d	3.88 m (SiH)[g]				
9-OCH_3	67–74 (0.05)		0.3–2.8 m[f]	0.03 d	3.90 m (SiH),[g] 3.83 s (OCH_3)	69.17	9.67	69.39	9.92
9-*p*-CH_3	63–65 (0.15)		0.3–2.8 m[f]	0.03 d	3.95 m (SiH),[g] 2.33 s ($ArCH_3$)	74.92	10.48	74.70	10.67
9-*m*-CH_3	63–67 (0.15)		0.2–2.8 m[f]	0.03 d	4.05 m (SiH),[g] 2.37 s ($ArCH_3$)	74.92	10.48	75.02	10.59
9-F	47–49 (0.4)		0.4–2.8 m[f]	0.03 d	4.0 m (SiH)	67.29	8.73	67.26	8.88
10-H[h]			0.49–2.6 m[f]	0.03 d	3.90 m (SiH)[g]	74.92	10.48	74.77	10.39

Table III (*Continued*)

compd	bp, °C (mm)	$CH_2Cl(Br)$	$SiCH_2CH_2$	^1H NMR, δ[a] $SiCH_3$	other	anal. calcd C	anal. calcd H	anal. found C	anal. found H
10-CH_3	70–75 (0.5)		0.3–2.8 m[f]	0.07 d	4.0 m (SiH),[g] 2.4 s ($ArCH_3$)	75.65	10.74	75.92	10.94

[a] For complete spectra, see ref 2. Aromatic protons for all compounds were in the range δ 6.8–7.9 m. The IR spectra have been omitted for brevity. However, for all compounds the characteristic absorptions associated with Ar–Si (6.25–7.02, 8.95–9.1 μM) and CH_3SiCH_3 (7.99–8.1, 11.4–12.65 μM) were observed. [b] Known compound. See Experimental Section. [c] $CH_2CH{=}CH_2$, J = 8 Hz. [d] CH_2OH. [e] All protons of the alkyl group. [f] All methylene protons (trioxane internal standard, δ 5.18). [g] Nonet, J = 3.6 Hz. [h] Collected by gas chromatography only.

carbonate solution and brine and dried ($MgSO_4$). Distillation produced a colorless oil (2.5 g, bp 109–110 °C at 0.2 mm) which, by spectral and GLC evidence, was ca. 70% δ-hydroxy-*n*-butyl-*p*-tolyldimethylsilane. Treatment of this alcohol in the tosylate-displacement procedure (see above) gave **6**-CH_3 in 35% yield (from the ether), identical in every respect with the product formed via hydrosilylation.

***n*-Propyl- and *n*-Butylsilanes, 7 and 8 (Procedure III-A).** Silane **7**-H was prepared as reported.[4] The other alkylsilanes were prepared similarly from the proper aryldimethylchlorosilane and either *n*-propyl- or *n*-butylmagnesium bromide, as described for the allylsilanes (procedure I-B). The yields follow: **7**-H (54%); **7**-OCH_3 (35%); **7**-CH_3 (32%); **7**-F (49%); **8**-H (45%); and **8**-CH_3 (40%).

Silicon Hydrides, 9 and 10 (Procedure III-B). 3-Phenyl-1-bromopropane was purchased from Aldrich and was used as received. The other aralkyl bromides were prepared by procedure I-C from the appropriate olefin, as indicated: 3-*p*-anisyl-1-bromopropane[33] from 3-*p*-anisylpropene;[34] 3-*p*-tolyl-1-bromopropane[33] from 3-*p*-tolylpropene;[35] 3-*m*-tolyl-1-bromopropane[33] from 3-*m*-tolylpropene;[36] and from 3-*p*-fluorophenylpropene[37] was prepared 3-*p*-fluorophenyl-1-bromopropane [49%, bp 50–51 °C at 0.35 mm; n_D (23 °C) 1.517; δ (CCl_4) 6.9–7.6 (m, ArH), 3.45 (t, J = 7 Hz, $-CH_2Br$), 2.90 (t, $ArCH_2$), 2.25 (quintet, 2-CH_2)].

Anal. Calcd for $C_9H_{10}BrF$: C, 49.80; H, 4.46. Found: C, 49.93; H, of the aqueous phase. The ether extract was washed with sodium 4.60.

The physical constants and spectra of these compounds were in agreement with those where reported. 4-Phenyl-1-bromobutane was made as reported,[38] as was 4-*p*-tolyl-1-bromobutane.[39] These aralkyl bromides were then converted to their Grignard reagents (**10**-H was prepared from the organolithium reagent). The Grignard reagent (0.023 mol) was then *added to* dichlorodimethylsilane (PCR, Inc., 3.0 g, 0.023 mol) in ether and the solution was stirred under reflux for 20 h. The precipitated magnesium salts were filtered off under nitrogen, and lithium aluminum hydride (0.5 g, 0.013 mol) was added to the filtrate. The solution was then refluxed for 15 h and processed by addition of wet ether, followed by diluted (1:1) hydrochloric acid. The ether phase was combined with several ether washes of the aqueous layer. After treatment with sodium bicarbonate solution, brine, and magensium sulfate, the ether was evaporated and the silicon hydride distilled. The yields follow: **9**-H (26%); **9**-OCH_3 (34%); **9**-*p*-CH_3 (34%); **9**-*m*-CH_3 (17%); **9**-F (30%); **10**-H (46%); and **10**-CH_3 (39%). For all silanes **7**–**10**, see Table III.

Reduction of Halosilanes with Tri-*n*-butyltin Hydride. The tin hydride (TBTH) was prepared as described.[40] Di-*tert*-butyl peroxide (DTBP) was distilled commercial material. Benzene was thiophene-free, distilled from sodium, and stored over 4A molecular sieves. The halosilanes were freshly collected GLC samples. Separate stock solutions of TBTH and DTBP in benzene were prepared. A weighed portion of the appropriate halosilane was dissolved in the proper volumes of the above solutions to make reaction mixtures in the ratios and concentrations given in Table I. Ten milliliters of the solutions so made was transferred to Vitro Cryules (25 mL, Wheaton Glass Co., Millville, N.J.). The cryules were subjected to three freeze–thaw degassing cycles, sealed under vacuum, and heated in a wax bath at 140 ± 5 °C for 20 h. The cryules were cooled and opened carefully, and the solution was distilled through a 4-in. Vigreux column to remove most of the benzene. The residue was analyzed by GLC at 150–180 °C using 20% Reoplex and 3% SE-30 columns. The samples of unrearranged and rearranged silanes so eluted were collected and authenticated by spectral (IR, NMR) comparison with knowns. The yields from the chlorosilanes were 90–95% based upon TBTH, as determined by use of separate calibration curves. The yields from the bromosilanes were lower (60–80%), reflecting the loss of product via further reaction with starting material (see eq 3 above). The rearrangement percentages were determined both from peak areas and by matching with synthetic mixtures of the knowns. All reactions were carried out at least twice and a few three times.

Control Experiments. Two sets of control experiments using GLC were performed for *each* aryl system and for *each* halogen: a test of stability of *reactants* to the various reaction components, and a similar test of the *products*. Reactant stability was tested by heating the appropriate halosilanes **1**, **4**, **5**, or **6** (10 mmol) with DTBP (1 mmol) under identical conditions with those used for the reductions. No reduction products were detected. Product stability was tested: (a) by heating silanes **7** or **8** (10 mmol) with TBTH (3 mmol) and DTBP (1 mmol) under reaction conditions. No rearranged silanes were found. (b) Various synthetic mixtures of unrearranged and rearranged silanes (10 mmol total) were heated with TBTH (3 mmol) under reaction conditions. No interconversion was detected.

For the *p-fluorophenyl cases* **1**-F and **4**-F, several revealing control experiments were conducted. (a) A benzene solution (ca. 1 mL) containing **1**-F (0.5 M), **4**-F (0.4 M), TBTH (0.49 M), and DTBP (0.16 M) was heated in a Carius tube (sealed under nitrogen) at 140 ± 2 °C for 12 h. Whereas the triplets for **1**-F (δ 3.55) and **4**-F (δ 3.40) were equally intense in the reactant NMR spectrum, only the δ 3.55 triplet remained in the product mixture, indicating total reduction of **4**-F. Analysis by GLC (OV-17, 180 °C) confirmed the absence of **4**-F and the essential nonreaction of **1**-F. Samples *at 25 °C* indicated that **4**-F was reduced in the mixture even upon standing for a few hours. Clearly the bromosilane was much more reactive than the chlorosilane. (b) A benzene solution (ca. 1 mL) containing **4**-F (0.54 M), 3-bromo-1-phenylpropane (γ-phenyl-*n*-propyl bromide, 0.53 M), TBTH (0.50 M), and DTBP (0.17 M) was treated as above. Analyses by NMR and GLC indicated that the bromides were reduced at essentially the same rate, both at 25 °C overnight and at 140 °C for 12 h. Bromosilane **4**-F thus showed no special reactivity in this regard. (c) Analogously, a benzene solution (ca. 1 mL) containing **1**-F (0.5 M), *n*-heptyl chloride (0.56 M), TBTH (0.53 M), and DTBP (0.25 M) showed no reduction at 25 °C but comparable reduction of the two chlorides at 140 °C for 12 h. So chlorosilane **1**-F showed no special nonreactivity in this regard. (d) Separate solutions of **1**-F (19 μL, 23 mg, 0.1 mmol) and **4**-F (17 μL, 27.5 mg, 0.1 mmol) in diphenyl ether (10.0 mL) were heated under nitrogen at 165–170 °C. After 10 min a mixture of TBTH (9 μL, 9.7 mg, 0.033 mmol) and DTBP (2 μL) was added to the hot solution via an injection by syringe through a septum. The final concentrations were those of 0.01 M halosilane in Table I. After 24 h at 165–170 °C the cooled solutions were analyzed by GLC (OV-17, 168 °C). Rearranged product **9**-F was easily detected in the case of **1**-F, but no **9**-F was observed from **4**-F. Unrearranged **7**-F was produced from both. Thus the disparity in rearrangement between chloro- and bromosilanes persists even when warmup is eliminated. (e) A benzene solution (ca. 1 mL) containing **4**-F (0.22 M), silicon hydride **9**-F (0.12 M), and DTBP (0.05 M) was heated in a Carius tube sealed under nitrogen at 140 ± 2 °C for 14 h. Analysis of the reaction mixture by GLC demonstrated that ca. 20% of reduced product **7**-F (based on consumed **9**-F) was formed. A separate test showed that no **7**-F formed when the reactant mixture itself was chromatographed. It was therefore shown that the rearrangement percentages from **4**-F (and undoubtedly all the bromosilanes) were too low (Table I) because of this subsequent reaction. (f) A study of **1**-F exactly as described above in (e) for **4**-F revealed no significant (<1%) formation of **7**-F, and the rearrangement values from **1**-F (and undoubtedly all the chlorosilanes) were therefore usable in the calculation or r and K_e.

Limit of Detection. By use of suitable mixtures of reaction com-

ponents on the scale employed, 3% rearrangement could be measured easily in these reductions by GLC. Rearrangement between 1 and 3% could be detected but not accurately measured.

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Kinetics of the Formation and Decomposition of Carbon–Cobalt(III) Bonds in Aqueous Solutions by the Reaction of Aliphatic Free Radicals with a Coenzyme B-12r Model Cobalt(II) Complex

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Abstract: The reactions of $\cdot CH_2OH$, $CH_3\dot{C}HOH$, $HO\dot{C}HCH_2OH$, and $\cdot CH_2CHO$ with a $Co^{II}L$ complex were studied (L = macrocyclic $Me_6[14]dieneN_4$). In all systems the product of these reactions is a $Co^{III}L$–RH complex. The mechanism of decomposition of these products depends on the nature of the aliphatic residue–RH. $Co^{III}L$–CH_2OH decomposes by a heterolytic cleavage of the carbon metal bond forming $Co^{I}L + CH_2O$. $Co^{III}L$–$CH(OH)CH_3$ seems to decompose by a hydride transfer from the β-carbon yielding $Co^{III}L$–H + CH_3CHO. $Co^{III}L$–$CH(OH)CH_2OH$ rearranges by loss of water to $Co^{III}L$–CH_2CHO, which then hydrolyzes to $Co^{III}L + CH_3CHO$. The latter reaction is a model reaction to that of the diol dehydratase enzyme which contains the coenzyme B-12. The mechanism of these reactions and their implication on the chemistry of other systems containing σ carbon–cobalt bonds are discussed.

The discovery that coenzyme B-12 is a cobalt(III) complex containing a cobalt–carbon bond initiated many studies concerning the mechanisms of formation and decomposition of these bonds.[1] One of the mechanisms leading to the formation of carbon–cobalt bonds is the reaction of free radicals with cobalt(II) complexes:[1-5]

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