Reduction of Halosilanes by Organotin Hydrides[1]

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Abstract: A study of the reduction of halosilanes with organotin hydrides is described. The free radical chain mechanism indicated by the results obtained parallels that known for the comparable reduction of haloalkanes, but the reactivity of α-halosilanes is considerably enhanced. Mechanistic studies suggest that the polar nature of the halogen abstraction step in the radical chain sequence, which places incremental negative charge adjacent to silicon, is the principal reason for this enhanced reactivity. Structure–reactivity studies indicate the *gem*-dimethylsilyl function to be an electronic transmitter. The ρ values for reduction of aryldimethyl(chloromethyl)silanes and substituted benzyl chlorides by tri-*n*-butyltin hydride are essentially identical (+0.45). Reduction of (chloromethyl)trimethylsilane with aryldimethyltin hydrides, conversely, yielded a ρ value of −1.61. The reduction produced racemic product from an optically active α-chlorosilane, the synthesis of which appears to be the first reported. Other syntheses of various halosilanes of interest are also described. The title reduction is specific for carbon–halogen bonds. Silicon–halogen bonds are not affected, a distinction that should make the reduction synthetically useful. Because the increased reactivity of α-halosilanes in this reduction has thus been ascribed to a kinetic polar effect in a critical step of the mechanism, no compelling argument for special thermodynamic stability in α-silyl radicals themselves can be made.

Over a period of time, results from this laboratory have indicated that α-silyl carbon-centered radicals $>$Si-C$<\cdot$ (henceforth "α-silyl" radicals) demonstrate differences from their all-carbon analogues.[2] First manifested in the absence of rearrangement of $Ph_3Si–CH_2\cdot$, a result which strongly contrasted with the near total rearrangement of $Ph_3C–CH_2\cdot$, the comparison of the two classes of radicals was continued in several other studies. Interest at that time centered upon rearrangement, and the conclusion reached was that vicinal rearrangement via a three-membered ring transition state was unknown in α-silyl radicals, contrary to its common occurrence with all-carbon radicals.[3] On the other hand, more distant rearrangement readily occurred with both classes. Among the possible explanations for this apparent resistance of α-silyl radicals toward such vicinal rearrangement was the interesting one of stabilization of such radicals by some type of odd-electron delocalization.[4] It was this possible stabilization of α-silyl radicals that led to the present study. Here the concern has been the *ease of formation* of α-silyl radicals relative to their all-carbon analogues, a kinetic feature. It was hoped that data of this type would bear upon the "stability"[5] of the α-silyl radicals. Of all the methods known for radical generation, few if any match the utility of the reaction of halides with organotin hydrides.[6] Herein, therefore, is reported the reaction of various halosilanes with special emphasis upon the similarities and differences between this reaction and its extensively documented counterpart in all-carbon systems.[7]

Table I. Relative Reactivities of α-Chlorosilanes and Chloroalkanes

$$R\text{-}Cl \xrightarrow[\substack{(AIBN) \\ 366nm \\ 35\text{-}40\,^\circ C}]{TBTH} R\text{-}H$$

1, Me_3SiCH_2	(1.0)
2, $(EtO)_3SiCH_2$	1.3
3, $PhSiMe_2CH_2$	1.7
4, Ph_3SiCH_2	4.5
5, $n\text{-}C_5H_{11}$	<0.01[c]
6, $neo\text{-}C_5H_{11}$	<0.01[c]
7, $t\text{-}Bu$	0.9

[a] Determined for equimolar mixtures of **1** and its competitor with 0.5 equiv of TBTH and 0.1 equiv of AIBN. [b] Products were isolated and confirmed for **1**, **3**, and **4**. [c] No reduction observed.

Table II. Relative Reactivities of Classes of α-Chlorosilanes

R (–Cl)	rel reactivity[a]
1 (1°)	(1.0)
14, $Me_3SiC(–)HMe$ (2°)	1.4
15, $Me_3SiC(–)HCH_2Me$ (2°)	1.8
16, $Me_3SiC(–)Me_2$ (3°)	4.1

[a] Cf. footnote *a*, Table I.

Scheme 1

$$ClCH_2CMe_2CH_2OH \xrightarrow{a} ClCH_2CMe_2CHO \xrightarrow{b}$$
$$\underset{8}{} \qquad\qquad \underset{9}{}$$

$$ClCH_2CMe_2CH=CH_2 \xrightarrow{c} ClCH_2CMe_2CH_2CH_2SiMe_2CH_2Cl$$
$$\underset{10}{} \qquad\qquad\qquad \underset{11}{}$$

[a] $(pyr)H^+ CrO_3Cl^-, CH_2Cl_2$, 80%. [b] $[Ph_3P=CH_2]$, Me_4SO, 30%. [c] $ClCH_2SiHMe_2, H_2PtCl_6$, 71%.

Results

The first item of investigation was the comparison of carbon vs. silicon substrates toward reduction with tri-*n*-butyltin hydride. The relative reactivities of a series of halosilanes and some organic halides were determined in competition experiments in the usual way.[8] In selected cases the product was isolated as well. The results are gathered in the sections and tables following, organized according to some pertinent structural feature.

(1) Portions of this work are taken from the Dissertation of F.G.B. (1981) and the M.S. Thesis of P.A.Z. (1981).

(2) Earlier work from this laboratory cited back to 1965: Wilt, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 5251. Wilt, J. W.; Chwang, W. K.; Dockus, C. F.; Tomiuk, N. M. *Ibid.* **1978**, *100*, 5534.

(3) Wilt, J. W. *Free Radicals* **1973**, *1*, 334.

(4) Wilt, J. W.; Kolewe, O.; Kraemer, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 2624. Possibilities include (d–p) π-type stabilization or involvement with the silicon–carbon σ* orbital. Cf.: Pitt, C. G. *J. Organometal. Chem.* **1973**, *61*, 51. For a contrary view (no stabilization) cf.; Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(5) For the present usage of such a term, cf.: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *3*, 13.

(6) From its discovery (van der Kerk, G. J. M.; Noltes, J. G.; Luitgen, J. G. A., *J. Appl. Chem.* **1957**, *7*, 366) to date, this reduction has been employed literally hundreds of times. Cf.: Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299; a summary from the leading worker in the field.

(7) The present study was generated from the work of Aznavoorian, P. M. M. S. Thesis (Loyola University of Chicago), 1974. Wilt, J. W.; Aznavoorian, P. M. *J. Org. Chem.* **1978**, *43*, 1285. The application of the hypothesis of α-silyl radical "stability" has had important further application: Creary, X. *J. Org. Chem.* **1980**, *45*, 280. Swenton, J. S.; Anderson, D. K.; Jackson, D. K.; Narasimhan, L. *Ibid.* **1981**, *46*, 4825. Chenard, B. L.; Slapak, C.; Anderson, D. K.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1981**, 179. Choi, J.-K.; Hart, D. J.; Tsai, Y.-M. *Tetrahedron Lett.* **1982**, 4745.

(8) Specifically, the approach used was that of: Hutchinson, M. J.; Mosher, M. W.; *J. Chem. Educ.* **1971**, *48*, 629.

Table III. Influence of Chloro Substituents on α-Chlorosilane Reactivity

R (–Cl)	rel reactivity[a,b]
1	(1.0)
19, ClMe$_2$SiCH$_2$	3.7
20, Cl$_2$MeSiCH$_2$	11
21, Cl$_3$SiCH$_2$	82
22, Me$_3$SiCHCl	67

[a] The relative reactivity was determined as in footnote *a*, Table I, but *indirectly* using first other ratios: 19 vs. 4; 20–22 vs. benzyl chloride. These values were then normalized to the standard 1, using 4 vs. 1 = 4.5 (Table I) and benzyl chloride vs. 4 = 7.8. [b] No evidence was found for SiH formation in any of these reductions.

α-Chlorosilanes vs. Chloroalkanes. Under the conditions employed, α-chlorosilanes exhibited considerable reactivity toward reduction by tri-*n*-butyltin hydride (TBTH). Contrariwise, primary chloroalkanes of corresponding structure were essentially inert, although *tert*-butyl chloride did show comparable behavior. It would seem that α-silyl primary chlorides are activated toward this reduction and reach the reactivity level demanded of tertiary chlorides in all-carbon examples. The data are given in Table I, with certain details reserved for the Experimental Section of this article.

With the clearly enhanced reactivity in mixed competition of α-chlorosilanes in this reduction with TBTH established, an internal competition in a model compound that combined both types of chloro functionality was devised to check this reactivity further. The synthesis of such a model compound, 1,6-dichloro-2,2,5,5-tetramethyl-2-silahexane (11), was achieved as shown in Scheme I.[9] The reduction of 11 led exclusively to reduction of the 1-chloro function (the α-chlorosilane end) to form 12 in essentially quantitative yield (eq 1). Both 12 and the alternative product

$$11 \xrightarrow[\substack{(AIBN)\\366\ nm}]{TBTH} ClCH_2CMe_2CH_2CH_2SiMe_3 \qquad (1)$$
$$\textbf{12}$$
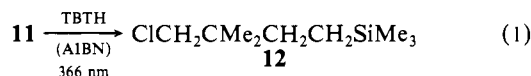
formed by reduction of the 6-chloro function, 1-chloro-2,2,5,5-tetramethyl-2-silahexane (13), were independently synthesized (see Experimental Section). Possible product 13 was not observed in the reduction of 11, within the sensitivity of the analyses (<5%).[10] Treatment of 11 with di-*tert*-butyl peroxide and TBTH at 135 °C gave the same result.

Reactivity among Classes of α-Chlorosilanes. Shown in Table II are the relative reactivities of primary, secondary, and tertiary α-chlorosilanes in the reduction with TBTH.

Chlorides 14 and 16 were available (see Experimental Section), but the previously unreported (1-chloropropyl)trimethylsilane (15) was prepared as shown in eq 2. Starting ketone 17 was itself

$$Me_3SiC(=O)CH_2Me \xrightarrow[86\%]{NaBH_4,\ alcohol}$$
$$\textbf{17}$$
$$Me_3SiCH(OH)CH_2Me \xrightarrow[78\%]{SOCl_2,\ ether} Me_3SiCH(Cl)CH_2Me \quad (2)$$
$$\textbf{18} \hspace{5cm} \textbf{15}$$

obtained by the unusual route recently described by Sakurai and co-workers.[11,12]

Influence of Chloro Substituents. The data in Table I indicated that the reactivity of α-chlorosilanes toward TBTH might be

Table IV. Miscellaneous Reductions

R (–Cl)	rel reactivity[a]
1	(1.0)
23, Me$_3$SiSiMe$_2$CH$_2$	7.7
24, CH$_2$=CHSiMe$_2$CH$_2$	1.6
25, CH$_2$=CHCH$_2$SiMe$_2$CH$_2$	1.7
26, Et$_3$SiC(–)HC$_6$H$_5$	115

[a] Determined as in footnote *a*, Table I, except that 26 was compared to 21, and thence to 1 via comparisons: 21 vs. benzyl chloride; vs. 4; vs. 1.

Table V. Effect of the Silicon Site

R (–X)	rel reactivity[a]
X = Cl	
1	(1.0)
27, Me$_3$SiCH$_2$CH$_2$	0.33
28, Me$_3$SiCH$_2$CH$_2$CH$_2$	<0.05
X = Br	
29, Me$_3$SiCH$_2$	(1.0)[b]
30, Me$_3$SiCH$_2$CH$_2$	0.56
31, Me$_3$SiCH$_2$CH$_2$CH$_2$	0.16

[a] See footnote *a* of Table I. [b] No accurate value for 29 vs. 1 was obtainable using direct competition, but indirect comparisons using 21 indicate a value >10^2.

Table VI. Reduction of ClCH$_2$CH$_2$SiMe$_2$CH$_2$Cl (33)[a]

initial concn[b]		final concn (6 h)				
TBTH	33	TBTH	33	34	27	35
520	500	0	86	47	280	87
570	520	0	73	45	283	119

[a] 366 nm, in benzene containing AIBN (10%). [b] In moles × 10^{-4}.

influenced by an electron-withdrawing substituent near the reaction zone. To investigate this feature of reactivity, a series of chloro-substituted α-chlorosilanes was reduced, with the results shown in Table III. One might note that *this reduction of α-chlorosilanes does not affect Si–Cl bonds*, in sharp distinction from reduction with lithium aluminum hydride, which behaves exactly oppositely. Such disparate behavior should be synthetically valuable.

Miscellaneous Competition Studies. Certain other functions were also studied in this α-chlorosilane competition portion of the study. The relative reactivities of these known substrates are given in Table IV. The synthesis of the new α-chlorosilane 26 is given later (vide infra).

Effect of the Silicon Site. The reactivity of α-chlorosilanes toward TBTH led to speculation that the position of the silicon affected this reactivity. The reactivity was therefore determined for more distant halosilanes. These results are gathered in Table V.
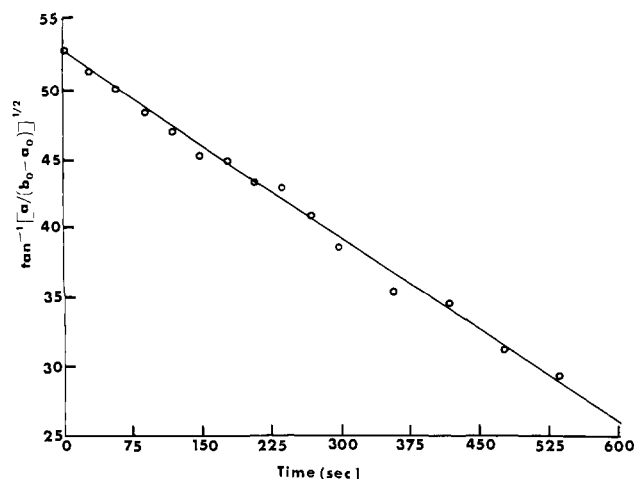
An internal competition was performed upon (2-chloroethyl)(chloromethyl)dimethylsilane (33), prepared as shown in eq 3. Reduction of 33 led to three products as shown in eq 4.

$$CH_2=CHSiMe_2CH_2Cl \xrightarrow{Hg(OAc)_2,\ THF,\ H_2O,\ NaBH_4,\ 56\%}$$
$$\textbf{24}$$
$$HOCH_2CH_2SiMe_2CH_2Cl \xrightarrow{SOCl_2,\ pyridine,\ ether,\ 76\%}$$
$$\textbf{32}$$
$$ClCH_2CH_2SiMe_2CH_2Cl \quad (3)$$
$$\textbf{33}$$

$$33 \xrightarrow[\substack{(AIBN)\\366\ nm}]{TBTH}$$
$$ClCH_2SiMe_2CH_2Me + ClCH_2CH_2SiMe_3 + MeCH_2SiMe_3$$
$$\textbf{34} \hspace{3cm} \textbf{27} \hspace{3cm} \textbf{35}$$
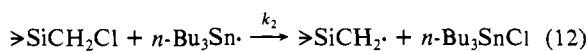$$(4)$$

The process was complicated by subsequent reduction of 34 and

(9) Some of this material was published earlier in communication form: Wilt, J. W.; Aznavoorian, P. M., ref 7.

(10) The same result has been observed with the tetraphenyl analogue of 11: Wilt, J. W.; Belmonte, F. G., unpublished work.

(11) Hosomi, A.; Hashimoto, H.; Sakurai, H. *J. Organomet. Chem.* **1979**, *175*, Cl.

(12) During the course of this study alcohol 18 was reported via a different route (Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* **1980**, *45*, 3571).

(13) Optically active organosilicon compounds chiral at Si, or Si *and* C, have been known for years and have been used in mechanistic studies. Cf.: Brook, A. G.; Bassindale, A. R. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed., Academic Press: New York, 1980; Vol. 2, pp 149–227.

Table VII. Halogen Effect in α-Halosilane Reactivity

halide pair	rel reactivity
X = Cl, 1/6	>10^2 ^{a}
X = Br, 29/n-C$_5$H$_{11}$Br	6.6
X = I, 37, Me$_3$SiCH$_2$I/n-BuI	1.5

^{a} This value is uncertain. Under the conditions employed, 6 is not reduced. Direct competitions studied by the NMR method do not assay accurately when the relative reactivities differ significantly (ca. >20-fold).

27 to **35**, and no quantitative dissection of rates was possible. However, as shown in Table VI, chloride **27** was the major product, showing that the α-chloro function was clearly the more reactive—as had been shown by external competition studies (Table V).

Another such study was carried out upon (α,β-dichloroethyl)trimethylsilane (**36**). Analysis by NMR spectroscopy manifested total reduction of the α-chloro functionality to produce **27**, with no discernible reduction of the β chlorine to produce **14** (eq 5).

Effect of Halogen on α-Halosilane Reactivity. To ascertain whether the marked reactivity of α-chlorosilanes toward TBTH would be maintained in the bromo and iodo analogues, competition studies were conducted as shown in Table VII.

Attention was next turned to *mechanistic* features of the reduction, for which the aforementioned described reactivity of the α-halosilanes was now well-documented. To be reasonably certain that the TBTH reduction of halosilanes was indeed a radical chain process, the effect of reaction conditions was investigated.

Effect of Additives (Initiators and Inhibitors). In Table VIII are collected the results of this portion of the study. The data in Table VIII clearly indicate that a chain process involving radicals is involved in the reduction of **1**. Such a process has implications with regard to other mechanistic features, as described next.

Effect of Wavelength. It was observed that the reduction of **1** (TBTH, no initiator) was faster at shorter wavelengths. Several studies using triphenyltin hydride (TPTH), triphenylgermanium hydride (TPGH), and triphenylsilane were also performed. The quantitative measurement of these wavelength and reactivity effects are discussed later in conjunction with the overall mechanism of the process. In summary, however, these studies indicated TPTH to be the most reactive reagent (shortest half-time) and triphenylsilane an essentially inert reagent toward **1**.

Stereochemistry. A radical chain process should result in racemization of a chiral reactive site. It was therefore of interest to test the reduction process upon such a chiral substrate. The synthesis of (α-chlorobenzyl)triethylsilane (**26**) in Scheme II represents the first reported example of an optically active α-chlorosilane where the chirality is carbon centered.[13] The synthesis had some worthwhile aspects and it will be discussed further herein.

Treatment of a sample of (−)-**26**, $[\alpha]^{27}_D$ −71.9°, with 1.2 equiv of tri-n-butyltin deuteride (TBTD) under the usual conditions (Table I) produced (α-deuteriobenzyl)triethylsilane (**40**) in 79% yield after purification, $[\alpha]^{25}_D$ −0.06 ± 0.01°. Chloride **26** was not racemized under these reaction conditions. Contrariwise, reaction of a sample of (+)-**26**, $[\alpha]^{25}_D$ = +36.2°, with lithium triethylborodeuteride (Super Deuteride)[14] in tetrahydrofuran led

(14) Registered trademark of the Aldrich Chemical Co.

Table VIII. Effect of Initiators and Inhibitors

additive	% Reduction of 1^a	
	2 h	6 h^b
none^c	32 (37)	83 (78)
AIBN^d	88^e	
DTBP^f	89^e	
benzoyl peroxide^d	20	40
galvinoxyl^d		2
hydroquinone^f	2	45
oxygen^g	7	58

^{a} Measured by NMR analysis for residual 1. Product studies have shown that 1 afforded tetramethylsilane essentially quantitatively in this reduction. ^{b} TBTH was still present after 6 h. ^{c} On a 1 mM scale, the reaction mixture of 1, TBTH, trioxane (internal standard) in molar ratio 1:1:0.33, and dry, thiophene-free benzene solvent was irradiated at 350 nm under nitrogen. For the parenthesized values the solution was purged with nitrogen for 25 s prior to irradiation. ^{d} 1 mol % additive was used. ^{e} TBTH was consumed within 2 h. ^{f} 1.5 mol % additive was used. ^{g} The solution was purged with oxygen for 2 min.

Scheme II

^{a} Pyridine, 91%. ^{b} t-BuLi, 56%. ^{c} Resolution via hydrogen phthalate ester and strychnine in CHCl$_3$; recovery via [(p-dimethylamino)phenyl] magnesium bromide. ^{d} SOCl$_2$, pentane, 25 °C, ~100%.

to **40** in 77% yield after purification, $[\alpha]^{25}_D$ = +0.38 ± 0.02°.[15] These reactions are shown in eq 6.

ρ–σ Studies. Earlier data (Tables I, III, and IV) indicated that substituents on the silicon affect reduction reactivity, although the magnitude of this substituent effect is frequently considerably less (~10^1) than that of the α-silicon site effect itself (>10^2). It was therefore decided to probe this substituent effect by the study of **41-X**, substituted aryldimethyl(chloromethyl)silanes ("sila-neophyl chlorides"). A series of such chlorides was prepared by coupling of arylmagnesium bromides and chlorosilane **19**, as shown in eq 7, with yields ranging from 14% to 55%. Because these

$$\text{X-C}_6\text{H}_4\text{MgBr} + \text{ClSiMe}_2\text{CH}_2\text{Cl} \xrightarrow[\Delta]{\text{ether}} \text{X-C}_6\text{H}_4\text{SiMe}_2\text{CH}_2\text{Cl}$$
$$\mathbf{19} \qquad\qquad\qquad\qquad\qquad \mathbf{41\text{-}X}$$
$$(7)$$

sila-neophyl chlorides were not readily distinguishable from the parent **3** (**41-H**) with respect to the individual CH$_2$Cl chemical shifts, their reactivities were contrasted with that of **1** and indirectly thence to **3**. This data is collected in Table IX. A Hammett plot of log (relative reactivity) vs. σ values from the data in Table IX gave ρ = +0.45, r = 0.9659. A similar Hammett–Brown plot vs. σ$^+$ values afforded ρ$^+$ = +0.31, r = 0.9247, obviously a somewhat comparable correlation.

It was also of interest to investigate the effect of substituents on the organotin hydride reactant. The first indication that halosilanes were susceptible to such substituents arose from use

Table IX. Relative Reactivity of X-C$_6$H$_4$SiMe$_2$CH$_2$Cl (41-X)

X	rel reactivity[a]
p-CF$_3$	2.14
m-CF$_3$	1.61
m-F	1.55
p-Cl	1.22
p-F	1.14
H (3)	(1.00)
p-t-Bu	0.98
m-CH$_3$	0.95
p-CH$_3$	0.92
p-OCH$_3$	0.86

[a] 366 nm, benzene solvent.

Table X. Relative Reactivity of (X-C$_6$H$_4$)Me$_2$SnH (42-X) toward 1

X	rel reactivity[a]
p-MeO	8.43
p-F	1.57
p-CH$_3$	1.54
H	(1.00)
p-CF$_3$	0.23

[a] At 300 nm, using solutions of 1 and the appropriate 42-X in isooctane.

of di-*n*-butylchlorotin hydride, *n*-Bu$_2$SnClH (DBCTH).[16] Direct competition for 1 by TBTH and DBCTH was not possible because the latter two hydrides undergo hydride–halogen exchange.[16] An indirect method, described in the Discussion section, led to a relative reactivity value of 0.054 for 1 with respect to reduction by DBCTH compared to TBTH. To probe this effect further, the reduction shown in eq 8 was studied. The tin hydrides 42-X

$$\text{Me}_3\text{SiCH}_2\text{Cl} + (\text{X-C}_6\text{H}_4)\text{Me}_2\text{SnH} \xrightarrow[\text{isooctane}]{300 \text{ nm}}$$
$$\quad\mathbf{1}\qquad\qquad \mathbf{42\text{-X}}$$
$$\qquad\qquad \text{Me}_4\text{Si} + (\text{X-C}_6\text{H}_4)\text{Me}_2\text{SnCl} \quad (8)$$

were prepared as given in eq 9 (Scheme III), and the reductions of 1 are tabulated in Table X. A Hammett plot of the data in Table X gave a value of $\rho = -1.61$, $r = 0.9087$. Again, as with 41-X, a comparable correlation was obtained from a Hammett–Brown plot, from which the value $\rho^+ = -1.10$, $r = 0.8713$, was obtained. Similar reductions of bromide 29 and iodide 37 were performed. With 42-H and 42-*p*-CF$_3$, iodide 37 was reduced too fast (within several minutes) to obtained reliable rate data. Interestingly, bromide 29 was reduced by 42-H and 42-*p*-OCH$_3$ at about the same rate (1:1.02), exemplifying the small effect of the substituent in 42-X in this case. This stands in contrast to this effect upon the reduction of 1 (Table X).

Kinetic Isotope Effect. Lastly, the mechanism of the reduction was investigated by using 1 and TBTH vs. TBTD. Again an indirect method was used, as discussed later herein. A value $k_\text{H}/k_\text{D} = 0.92$ was found for 1 against these two stannanes. With (bromomethyl)trimethylsilane (29), a k_H/k_D value = 2.6 was found in analogous fashion.

Discussion

The most salient feature of the study is the noteworthy reactivity of α-halosilanes, especially α-chlorosilanes, toward reduction with TBTH.[17] No general quantitative measurement of the reactivity increment due to α-silicon in these halides compared to haloalkanes is available. Primary chloroalkanes were simply not reduced under the conditions used, and the competition technique used to obtain the relative reactivity data in this study fails in such a circum-

Scheme III

$$\text{Me}_2\text{SnCl}_2 \xrightarrow{a} (\text{X-C}_6\text{H}_4)_2\text{SnMe}_2 \xrightarrow{b} (\text{X-C}_6\text{H}_4)\text{Me}_2\text{SnI} \xrightarrow{c}$$
$$\qquad\qquad\quad \mathbf{36\text{-X}}\qquad\qquad\qquad \mathbf{37\text{-X}}$$

$$\qquad\qquad\qquad\qquad (\text{X-C}_6\text{H}_4)\text{Me}_2\text{SnH} \quad (9)$$
$$\qquad\qquad\qquad\qquad\qquad \mathbf{42\text{-X}}$$

[a] X-C$_6$H$_4$MgBr, ether (65–80%). [b] I$_2$, CCl$_4$, 25 °C (40–69%). [c] LiAlH$_4$, ether (38–58%).

stance. From Table I, the comparable reactivity of *tert*-butyl chloride (7) and (chloromethyl)trimethylsilane (1) indicates, however, that *the α-silicon function raises the reactivity level of primary α-chlorosilanes to that of tertiary chloroalkanes*. If the processes were comparable mechanistically, this would imply a factor of ca. 20-fold increased reactivity in α-chlorosilanes.[19] At the outset of this work, two mechanisms were postulated to account for this unusual reactivity: the first, a radical chain process comparable to the known carbon case;[6] the second, a hydride displacement mechanism of the S$_\text{N}$2 type. The data in the tables given above show clearly that the latter is not operative. The conclusions, stated briefly, from these tables are given in turn.

Table II shows that the class of α-chlorosilane is a minor consideration, with tertiary α-chlorosilane 16 having only a 4-fold increase in reactivity relative to the standard primary α-chlorosilane 1. Importantly, reactivity increased with 16, a point against a hydride displacement mechanism but in keeping with the trend known for the radical mechanism of the all-carbon series.[6]

Table III shows the strong influence of chlorine substituents on the reduction. Greatest reactivity is observed with *geminal* substitution (22) while the *vicinal* effect increases ca. 4-fold with each chlorine [reactivities of $\mathbf{1:19:20:21} \cong 1:(4.3)^1:(4.3)^2:(4.3)^3$], the effect being multiplicative. Again, such an effect is known in the carbon process[6] and further implicates a radical mechanism for these reductions.

Table IV gives examples of further substrates of interest. The similar reactivity of 24 and 25 may well reflect the ambivalent nature of the vinyl group in the former.[21] Apparently the electron-donating and -withdrawing power of this function are in near balance. The net result could be a mild electron-withdrawing contribution essentially equal to that of the allyl function. In 23 the pentamethyldisilyl function serves as one of the more potent activating groups, an interesting result that will be referred to later. With 26, its benzylic nature dominated its high reactivity, although the α-silicon effect was apparent as well.[22]

Tables V and VI implicate *the position of the silicon as critical for reactivity*. The attenuation of reactivity with increasing distance of the silicon site is more pronounced in the chloro series than in the bromo series, because alkyl bromides are known to be vastly more reactive toward TBTH than are chlorides. It is, therefore, expected that the added influence of silicon (perhaps 20-fold) would be less.

Table VII further exemplifies the above conclusion. Adding extra reactivity (e.g., a factor of $<10^2$) to substrates that are already extremely reactive toward TBTH produces a less dramatic change. In the alkyl halides, for example, the relative reactivities of the halides are Cl:Br:I $\cong 1:10^4:10^6$.[20] If ΔR be the increased reactivity due to the α-silicon effect, then the relative reactivities would rise to $1 + \Delta R$: $10^4 + \Delta R$: $10^6 + \Delta R$, i.e., a correspondingly less significant increment with the more reactive bromides and iodides.

Table VIII, a most significant set of data, clearly *establishes the radical and chain nature* of the reduction. The poor initiation by benzoyl peroxide is undoubtedly caused by the induced decomposition of this peroxide by tin radicals[23] (in contrast to azo

(16) Sawyer, A. K.; Brown, J. E.; Hanson, E. L. *J. Organomet. Chem.* **1965**, *3*, 464.

(17) For reasons as yet unknown, use of the expectedly reactive[18] hexa-*n*-butyl- or hexaphenylditin (in hydrogen donor solvents) failed to reduce α-chlorosilanes: Wilt, J. W.; Paukner, J., unpublished work.

(18) Kuivila, H. G.; Pian, C. H.-C. *J. Chem. Soc., Chem. Commun.* **1974**, 369.

(19) Abstraction of chlorine from *t*-BuCl by *n*-Bu$_3$Sn· at 25 °C is 19 times faster than from *n*-pentyl chloride.[20]

(20) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

(21) Reynolds, W. F.; Modro, T. A.; Mezoy, P. G.; Skorupowa, E.; Maron, A. *Can J. Chem.* **1980**, *58*, 412.

(22) Chloride 26 is 3.4 times as reactive as benzyl chloride.

(23) Rubsamen, K.; Neumann, W. P.; Sommer, R.; Frommer, U. *Chem. Ber.* **1969**, *102*, 1290.

Figure 1. Kinetic plot for the photoinitiated (254 nm) reduction of (chloromethyl)trimethylsilane (1) by tri-*n*-butyltin hydride (TBTH) in the absence of added initiator. Case 1: $[1]_0 = 0.743$ M; $[TBTH]_0 = 0.471$ M. Dimethyl carbonate was the NMR internal standard. TBTH consumption over the time shown was 82%.

Figure 2. Kinetic plot for the photoinitiated (366 nm) reduction of (chloromethyl)trimethylsilane (1) by tri-*n*-butyltin hydride (TBTH) in the absence of added initiator. Case 2: $[1]_0 = 0.406$ M; $[TBTH]_0 = 0.593$ M. Dimethyl carbonate was the NMR internal standard. TBTH consumption over time shown was 38%. Note the induction period to ca. 2400 s.

compounds and dialkyl peroxides which do not undergo such induced decomposition). The reactions with hydroquinone and oxygen illustrate an induction period, wherein the inhibitors are effective. After this time the inhibitors were presumably consumed and the normal chain sequence then proceeded. The chain length of the sequence is apparently quite large because 1 mol % of galvinoxyl effectively stopped the reduction over a 6-h reaction time.

From all of the above data and the conclusions reached therefrom, a provisional chain sequence could be reasonably posited, as shown in eq 10–15.[24–26] For the reductions performed in the

$$\text{initiator} \xrightarrow{h\nu} \text{r}\cdot \tag{10}$$

$$\text{r}\cdot + \text{TBTH} \rightarrow \text{rH} + n\text{-Bu}_3\text{Sn}\cdot \tag{11}$$

$$\text{>SiCH}_2\text{Cl} + n\text{-Bu}_3\text{Sn}\cdot \xrightarrow{k_2} \text{>SiCH}_2\cdot + n\text{-Bu}_3\text{SnCl} \tag{12}$$

$$\text{>SiCH}_2\cdot + \text{TBTH} \xrightarrow{k_3} \text{>SiCH}_3 + n\text{-Bu}_3\text{Sn}\cdot \tag{13}$$

$$(12), (13), (12), (13), \text{etc.} \tag{14}$$

$$2n\text{-Bu}_3\text{Sn}\cdot \xrightarrow{k_4} n\text{-Bu}_3\text{SnSn-}n\text{-Bu}_3 \tag{15}$$
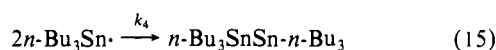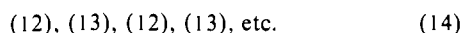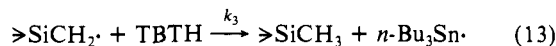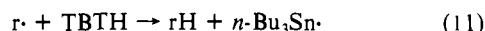
absence of an initiator, termed the "self-initiated reduction", primary initiation (eq 10) would be replaced by either eq 16 or 17. The ultraviolet spectra of TBTH and 1 were determined

$$\text{TBTH} \xrightarrow[k_1]{h\nu} n\text{-Bu}_3\text{Sn}\cdot + \text{H}\cdot \tag{16}$$

$$\text{>SiCH}_2\text{Cl} \xrightarrow{h\nu} \text{SiCH}_2\cdot + \text{Cl}\cdot \tag{17}$$
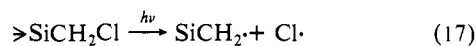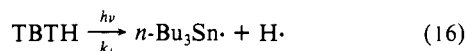
separately and as mixtures in isooctane. Only the former showed absorption above 300 nm (see Experimental Section), and it is therefore believed that eq 16 is the primary initiation step in the absence of AIBN or DTBP. Evidence for this belief was obtained by kinetic analysis of the "self-initiated" reduction of 1 by TBTH. By means of the steady-state approximation, it may be shown that

Table XI. Wavelength Dependence of the Self-Initiated Reduction[a]

$$1 + \text{TBTH} \xrightarrow[h\nu]{\text{isooctane}} \text{Me}_4\text{Si} + \text{TBT-Cl}$$

case	λ, nm	$10^4 k_T$, s^{-1} M$^{-1/2}$
1	366	1.52 ± 0.023
	366[b]	1.35 ± 0.019
	366[c]	2.16 ± 0.013
	300	3.28 ± 0.059
	254	13.3 ± 0.17
2	366	0.77 ± 0.050[d]
	366[b]	0.87 ± 0.025

[a] See Experimental Section for details. [b] Duplicate run. [c] Triphenyltin hydride (TPTH) was used. [d] Because k_T is a compsoite of photochemical factors as well as several rate constants, there is no necessity that case 1 and case 2 need give the same k_T value.

the integrated three-halves order rate laws shown in eq 18 and 19 may be derived for a radical chain sequence by using k_1-k_4 of the above equations.

Case 1: Let $[TBTH]_0 = a_0 < [1]_0 = b_0$; $a = [TBTH]_t$, $b = [1]_t$; I = intensity of light; f = fraction of light absorbed; and $k_T = \frac{1}{2}(k_1 k_2^2 I f / 2 k_4)^{1/2}$. Then,

$$\tan^{-1} [a/(b_0 - a_0)]^{1/2} =$$
$$-k_T(b_0 - a_0)^{1/2}t + \tan^{-1} [a_0/(b_0 - a_0)]^{1/2} \tag{18}$$

Case 2: $a_0 > b_0$; all symbols as in Case 1. Then,

$$\ln [a^{1/2} - (a_0 - b_0)^{1/2}]/[a^{1/2} + (a_0 - b_0)^{1/2}] = -2k_T(a_0 - b_0)^{1/2}t + \ln [a_0^{1/2} - (a_0 - b_0)^{1/2}]/[a_0^{1/2} + (a_0 - b_0)^{1/2}] \tag{19}$$

For Case 1, plots of $\tan^{-1} [a/(b_0 - a_0)]^{1/2}$ vs. time gave "good" straight lines for which the slope (in deg s^{-1}) $= -k_T(b_0 - a_0)^{1/2}$. A typical example is given in Figure 1. Division of the slope by $-(b_0 - a_0)^{1/2}$ and adjustment of units by multiplication by 2π rad/360° gave the composite constant k_T (in s^{-1} M$^{-1/2}$). For Case 2, plots of $\ln [a^{1/2} - (a_0 - b_0)^{1/2}]/[a^{1/2} + (a_0 - b_0)^{1/2}]$ vs. time also gave good straight lines where the slope (in s^{-1}) $= -2k_T(a_0 - b_0)^{1/2}$, which when divided by $-2(a_0 - b_0)^{1/2}$ again gave k_T (in s^{-1} M$^{-1/2}$). An example of such a plot is shown in Figure 2. Clearly k_T is not dissectable with present information but it may be used, for example, to compare different substrates or to investigate the influence of wavelength. The wavelength kinetic data for reductions carried out in the absence of initiators (the "self-initiated reduction") are collected in Table XI.

For several of the runs in Table XI induction periods of variable length (at times as long as 1 h) were observed. These variable

(24) A comparable mechanism involving *electron transfer* in the halogen abstraction step cannot be distinguished by our work from that given. For such a mechanism at work with trialkyltin hydrides, cf.: Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1557, and references therein.

(25) For a recent study of eq 13 with alkyl radicals, cf.: Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739. We have no data at present for the rate constant of eq 13.

(26) Assuming that the $D(CCl)$ values in α-chlorosilanes and chloroalkanes are comparable, the overall ΔH values for the two reduction processes would also be comparable (ca. −40 kcal mol^{-1}).[20]

induction periods are believed to be caused by adventitious oxygen, a known inhibitor (Table VIII). Clearly, as the wavelength used approached the absorption region of TBTH [λ_{max} 248 nm (broad) at 0.8 M, the concentration region used for these reactions], the reduction rates increased. While the intensity (I) increased with such a wavelength change, the fraction absorbed (f) is probably the more important factor, causing k_1 to increase. The excellent linearity observed for these reductions at different wavelengths when graphed by eq 18 and 19 lends powerful support to the mechanism given in eq 16 and 12–15, the self-initiated reduction. Equations were also developed for a chain sequence where 1 was made the initiator and other termination steps were assigned. No linear correlation with the reduction rate data was found with these equations. When initiators (AIBN or DTBP) were employed, the reductions were much faster, of course. In such cases it is reasonable to assume that primary initiation now is eq 10. For AIBN this is reasonable because the 366-nm light used is close to its absorption maximum (345 nm). The usefulness of DTBP at 366 nm may be due to its very broad ultraviolet absorption caused by a dissociative singlet state. The broad absorption extends into the 366-nm region and allows the photoinitiation observed.[27]

The radical mechanism for reduction is also supported by the stereochemistry of the reduction, viz., *racemization at a chiral reaction center* (see Results). To achieve this result, the synthesis of optically active chloride 26 was required. The procedure of West[28] was used to prepare alcohol 39. At the scale used, even with extended reaction times and increased concentrations of *tert*-butyllithium, the conversion of silyl ether 38 to 39 was incomplete. However, separation of the two was easily achieved when the latter was converted to its hydrogen phthalate ester. The major problem in the synthesis was the hydrolysis of these esters, once resolved, back to active 39. The failures are briefly described in the Experimental Section. Treatment with [(p-dimethyl-amino)phenyl]magnesium bromide was eventually discovered to be an ideal cleavage. As shown in eq 20, the byproduct phthalide

$$39 + \quad \xrightarrow{H^+} \quad salt \quad (20)$$

43 (Ar = p-N,N-Me$_2$NC$_6$H$_4$)
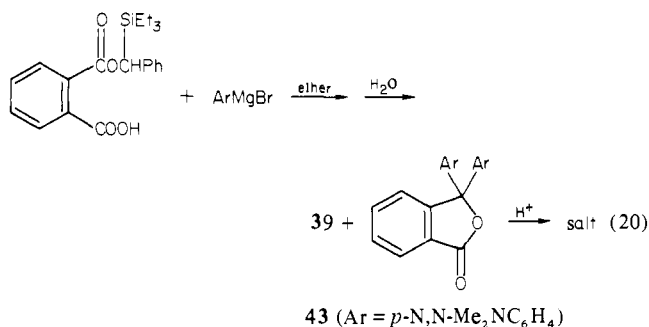
43 was easily removed with acid. Alcohols 39 (+ and −) were assayed for optical purity with shift reagents. Such studies were also attempted on the chlorides 26 and the silanes 40 (see Experimental Section).

The problem in such studies of reductions is whether or not a chiral product could be detected were it formed. This is particularly true for alkane- or arene-type products, for which low specific rotations are expected. It was gratifying to observe measurable activity in silane 40[15] when Super Deuteride[14] was used (eq 6). This allows the racemization observed with TBTD to be meaningful mechanistically. The inversion claimed for Super Deuteride,[14] though not proved, is reasonable in light of the high S_N2 reactivity of this reagent.[29]

The radical chain mechanism for the reduction having been established, the heart of the matter remained to be rationalized. Why are α-halosilanes (particularly α-chlorosilanes) so reactive compared to alkyl analogues? A clue surfaced when the lowered

reactivity of DBCTH compared to TBTH was measured (0.054:1.00). Because a mixture of TBTH and DBCTH disproportionates,[16] a direct competitive study of their reduction of 1 was not possible. Therefore this reactivity was measured by using certain data for 7 along with 1 by an indirect method which assumes that abstraction of chlorine by the organotin radical is the crucial step and that radical concentrations are equal. The equation used is shown (eq 21), in which the first two terms are

$$R = \frac{k_D[1][D\cdot]}{k^0[7][D\cdot]} \frac{k^*[7][T\cdot]}{k_T[1][T\cdot]} \frac{k^0[7][D\cdot]}{k^*[7][T\cdot]} = \frac{k_D[1][D\cdot]}{k_T[1][T\cdot]} =$$
$$(0.25)(0.9)(0.24) = 0.054 \quad (21)$$

R = relative reactivity of 1 toward reduction by DBCTH vs. TBTH; D· = n-Bu$_2$ClSn·; T· = n-Bu$_3$Sn·; k^* = 1.6×10^4 M^{-1} s^{-1} [20]; k^0 = 3.9×10^3 M^{-1} s^{-1} [20]

values measured in direct competitions of 1 vs. 7 with limited amounts of DBCTH and TBTH, respectively. The last term is based upon literature data for *tert*-butyl chloride in its reaction with these two tin hydrides. It should be emphasized that the value 0.054 for 1 is a relative value actually based on the value of 0.24 for 7. This result indicated that possible substituent effects could be further probed, using more conventional approaches.

The structure–reactivity studies (ρ–σ studies) bear on this aspect directly. The ρ value (+0.45) for reduction of chlorides 41-X by TBTH is close to the value for such reduction of benzyl chlorides (+0.40,[30] +0.40,[31] and +0.42[32]). Additionally, for the first time, quantitative determination of the substituent effect from the "other end" of the system, the tin hydrides 42-X, has beem made. Two items of interest arise from these studies.[33] First, the signs of ρ differ, positive at the organosilicon end and negative at the tin hydride end. Second, comparable correlations with either σ or σ^+ values were found for 41-X and 42-X. From a commonly accepted[34] description of the chlorine-abstraction step with alkyl chlorides and TBTH, eq 22, one may now pinpoint the influence

$$RCH_2Cl + \cdot SnR_3' \rightarrow [R\overset{\delta-}{C}H_2\text{---}\overset{\delta+}{C}l\text{---}SnR_3'] \rightarrow$$
$$RCH_2\cdot + ClSnR_3' \quad (22)$$
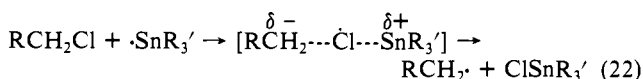
of the α-silicon function. For the present study, eq 22 becomes eq 23. It is believed that *the ability of silicon to stabilize adjacent*

$$>SiCH_2Cl + \cdot SnR_3' \rightarrow [\equiv Si\overset{\delta-}{C}H_2\text{---}\overset{\delta+}{C}l\text{---}SnR_3'] \rightarrow$$
$$>SiCH_2\cdot + ClSnR_3' \quad (23)$$
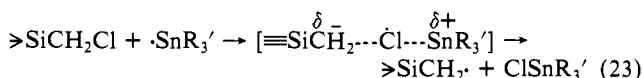
electron rich centers contributes significantly to the reactivity of the α-halosilanes.[36] This polar effect in the transition state, well recognized in all reductions with TBTH,[38] is thus augmented with α-halosilanes. Manifestly, as the silicon is removed farther from

(27) We thank a referee for this information. The reported UV spectrum of DTBP lists ϵ 0.9 (305 nm), 7.1 (245 nm). Cf.: Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; pp 443–450.

(28) West, R.; Lowe, R.; Steward, H.; Wright, A. *J. Am. Chem. Soc.* **1971**, *93*, 282.

(29) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669.

(30) Wilt, J. W., unpublished work.

(31) Blackburn, E. V.; Tanner, D. D. *J. Am. Chem. Soc.* **1980**, *102*, 692.

(32) Migira, T.; Machida, T.; Nagai, Y. Abstr. 21st Annual Meeting of the Chemical Society of Japan, Tokyo, 1968, Abstr. 111, p 1955.

(33) Admittedly, small absolute values for ρ do not lend themselves to definitive discussion. Nonetheless, gross effects germane to structure vs. reactivity may be discerned.

(34) By no means is the "direct abstraction" view in eq 22 universally accepted. The process may involve electron transfer (especially with iodides)[31] or an expanded halogen valence (as proposed for attack by triethylgermyl radicals).[35]

(35) Sakurai, H.; Mochida, K. *J. Organomet. Chem.* **1972**, *42*, 339.

(36) Another feature that may be involved is the relative *ground state* stability of α-chlorosilanes vis-a-vis chloroalkanes. The former are destablized relative to the latter as demonstrated by halide exchange reactions.[37] Aside from possible α-silyl stabilization of the transition state for chlorine abstraction (eq 23), such a ground state effect could contribute in and of itself to the increased reactivity of α-chlorosilanes. Because α-bromo- and α-iodosilanes show increased ground-state stability, their reactivity toward TBTH would correspondingly lessen and approach that of the haloalkanes, as observed. We thank Professor Peterson for a preprint and personal discussions on this point.

(37) Peterson, P. E. *Tetrahedron Lett.* **1981**, *22*, 1295.

(38) Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47.

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the reaction zone, this effect would decrease, thus explaining the importance of the silicon site (Table V). Such a polar effect, moreover, explains the sign of ρ for both **41**-X and **42**-X as well as the effect of electron-withdrawing substituents (rate increasing) on the organosilicon substrate and the tin hydride (rate decreasing). Moreover, this effect would be greatest when the substituent is closest (**22**) or when the number of such substituents increases (**21**). Additionally, σ^+ values could be appropriate for **41**-X, where conjugation of substituent X in $C_6H_4(X)$ with the carbon reaction site may be present, as shown by the comparable ρ values for **41**-X and benzyl chlorides. It would thus appear that *the dimethylsilyl function is an electronic transmitter*, essentially allowing direct interaction of the aryl group with the CH_2Cl function. The ability of σ^+ values to correlate the reactivity of **42**-X is reasonable, in that conjugative effects here seem quite plausible. This effect is the probable cause of the greater reactivity of TPTH (Table XI) vs. TBTH as well, because phenyl can exert a cation-stabilizing effect $(+R)$ on the tin even in the face of its mild destabilizing effect $(-I)$. TPTH is also more reactive toward **1** than is triphenylgermanium hydride (TPGH) or triphenylsilane (which is essentially unreactive under the conditions used here).[39,40] At 366 nm, with initiation by AIBN, the initial concentration of **1** was halved in 10 and 40 min by TBTH and TPGH, respectively. Contrariwise, little difference has been observed between **1**, Me_3SnCH_2Cl, and Et_3PbCH_2Cl (reactivities within 2-fold of each other).[30] Presumably all the group 4 α-halides would be *even more reactive* were it not for the opposition to the above polar effect caused by the electropositive character of the metal(oid) present. The rate acceleration caused by the pentamethyldisilyl function in **23** (Table IV) may be explained by invoking *further* delocalization of the anionic charge at the carbon reaction center (eq 23) through the d orbitals of both silicons, as shown in eq 24.

$$23 \cdot \; + \; TBT-Cl \quad (24)$$
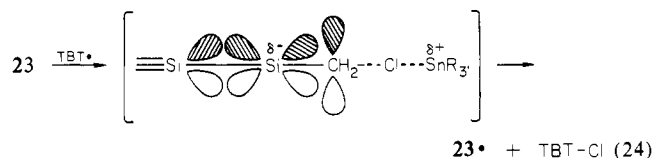
Alternatively, *hyperconjugation* involving the α-disilyl function and the $^{\delta-}CH_2\cdots Cl$ group in the transition state may be involved. Recent theoretical[43a,b] and experimental[43b] findings in α-silyl cations and anions in fact tend to support this view rather than that shown in eq 24, although admittedly the situation is not clear at present.[4]

The above rationale for α-chlorosilane reactivity rests upon the assumption that chlorine abstraction is the slow step of the chain. This assumption is justified by the kinetic isotope studies of **1** and **29** with TBTH vs. TBTD. The k_H/k_D values found (~ 1 and 2.6, respectively) are the same as those observed for alkyl halides[20] and indicate that the α-halosilanes behave analogously to the alkyl halides. For the chlorides, chlorine abstraction (eq 20 and 21) *is* rate determining, whereas for bromides and iodides the process is more complicated and involves halogen abstraction and/or transfer with TBTH as rate-determining step(s). It should therefore be emphasized that α-halosilane reactivity in these reductions depends upon the slow step of the sequence. Moreover, α-silyl radical "stability" is not necessarily involved. *What is*

necessary for α-silyl activation of a radical process is a polar factor in the transition state of the slow step with which the silicon can cooperate.

For this reason the reductions of bromide **29** and iodide **37** with the substituted tin hydrides **42**-X should not be compared directly with that of chloride **1**.[36] Probably the lack of a substituent effect in the reduction of **29** by **42**-X is caused by a change in the rate-determining step, i.e., from k_2 (eq 12) to k_3 (eq 13).

Lastly, mention should be made about the indirect method used to obtain the k_H/k_D values. The method employed the relation given in eq 25 and 26

$$(k_H/k_D)_1 = xyz = (1.1 \pm 0.11)(1.0)(0.833 \pm 0.083) =$$
$$0.92 \pm 0.18 \quad (25)$$

where x = the relative reactivity of **1** vs. **7** toward TBTH (Table I, $\pm 10\%$), $y = (k_H/k_D)_7$,[20] and z = the relative reactivity of **7** vs. **1** toward TBTD ($\pm 10\%$, determined as in Table I but with TBTD).

$$(k_H/k_D)_{29} = xyz = (0.94 \pm 0.94)(2.7)(1.04 \pm 0.104) =$$
$$2.6 \pm 0.3 \quad (26)$$

where x = the relative reactivity of **29** vs. *tert*-butyl bromide (**44**) toward TBTH ($\pm 10\%$, determined as in Table I), $y = (k_H/k_D)_{44}$,[20] and z = the relative reactivity of **44** vs. **29** toward TBTD ($\pm 10\%$, determined as in Table I but with TBTD).

Conclusion

The reduction of halosilanes with organotin hydrides follows the same free radical chain mechanism as the corresponding reduction of haloalkanes. The enhanced reactivity of α-halosilanes is ascribed principally to the ability of silicon to stabilize the transition state for halogen abstraction by a polar effect, wherein the partial negative charge on the carbon site is delocalized into (and through) the adjacent d orbitals of silicon. Such an explanation does not require that α-silyl radicals be stabilized relative to their all-carbon analogues. Further work must be carried out to investigate this aspect, and we are presently so engaged.

Experimental Section

Melting points were taken on a calibrated Fisher–Johns block. Boiling points are uncorrected. Spectra were taken on the following instrument models: IR, Perkin-Elmer 700 (only structurally significant absorptions are given in cm^{-1}); UV, Perkin-Elmer 575 (1-cm quartz cells); and ^1H NMR, Varian EM 360 (resonances are given in δ units, $Me_4Si = 0.00$). For some organosilanes standards other than Me_4Si (usually trioxane) were used in order to observe the upfield region more accurately. Polarimetry employed Polyscience SR6 ($\pm 0.1°$) or Rudolph Autopol III[15] ($\pm 0.001°$) instruments. Gas chromatography (GC) was conducted on either Hewlett-Packard 5750 or Gow-Mac 550 chromatographs using helium as the carrier gas. The usual column substrate was SE-30, 15% on Chromosorb P. Photochemical reactions were performed in NMR tubes (Norell, Inc., Pyrex >300 nm, quartz <300 nm). The irradiators used were a Bradford Scientific unit (254 and 366 nm) or a Southern New England Rayonet 400 Mini-reactor (300 nm). Elemental analyses were done by Micro-Tech Laboratories, Skokie, IL. Excepting those synthesized, all chemicals used in the study were commercial products, used as received if spectrally acceptable; otherwise the chemicals were purified by distillation or recrystallization. The petroleum ether used was the 30–60 °C bp material. Known compounds synthesized that had properties consonant with literature values were: TBTH,[44] TBTD (prepared as for TBTH but from $LiAlD_4$), **4**,[4] **16**,[45] **23**,[46] **27**,[47] **30**,[45] **31**,[48] **34**,[49] **35**,[50] **36**,[45] **37**.[51] Other literature citations to known compounds syn-

(39) At 135 °C over 4 h in the presence of DTBP, triethylsilane *did* reduce α-chlorosilanes. The relative reactivity **4/1** = 1.8 (compare the value 4.5 with TBTH at 35–40 °C in Table 1). Wilt, J. W., unpublished work.

(40) It should be stressed that the lessened reactivity of silanes as reducing agents may reflect differences in initiation rates. Abstraction of halogen from alkyl halides by $Et_3Si\cdot$ is actually *faster*[41] than with *n*-$Bu_3Sn\cdot$, a fact that may reflect the greater strength of SiCl vs. SnCl (104 vs. 94 kcal mol^{-1}, respectively[42]).

(41) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123.

(42) Sakurai, H. *Free Radicals* **1973**, *2*, 743.

(43) (a) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998. (b) Stang, P. J.; Ladika, M.; Apeloig, Y.; Stanger, A.; Schiavelli, M. D.; Hughey, A. *J. Am. Chem. Soc.* **1982**, *104*, 6852. We thank a referee for calling our attention to this work.

(44) Kuivila, H. G.; Beumel, O. F. *J. Am. Chem. Soc.* **1961**, *83*, 1246.

(45) Sommer, L. H.; Bailey, D. L.; Goldberg, G. M.; Buck, C. E.; Bye, T. S.; Evans, F. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1954**, *76*, 1613.

(46) Kumada, M.; Nakajima, J.; Ishikawa, M.; Yamamoto, Y. *J. Org. Chem.* **1958**, *23*, 292.

(47) Sommer, L. H.; Baughman, G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3346.

(48) Sommer, L. H.; Van Strien, R. E.; Whitmore, F. C. *J. Am. Chem. Soc.* **1949**, *71*, 3056.

(49) Petrov, A. D.; Mironov, V. F.; Pogonkina, N. A. *Dokl. Akad. Nauk SSSR* **1955**, *100*, 81; *Chem. Abstr.* **1956**, *50*, 1573.

(50) Whitmore, F. C.; Sommer, L. H.; DiGiorgio, P. A.; Strong, W. A.; Van Strien, R. E.; Bailey, D. L.; Hall, H. K.; Pietiusza, E. W.; Kerr, G. T. *J. Am. Chem. Soc.* **1946**, *68*, 475.

(51) Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481.

thesized in this study will be given in their appropriate section (vide infra).

Syntheses. 1,6-Dichloro-2,2,5,5-tetramethyl-2-silahexane (11). Chloropivaldehyde (**9**) was prepared from chloro alcohol **8** (Aldrich) by oxidation with pyridinium chlorochromate in the usual way (80%, short-path distillation, bath 100 °C (150 mm), lit.[52] bp 80 °C (15 mm)). The 2,4-DNP was prepared in standard fashion: yellow needles from alcohol, mp 137–138 °C (some samples had mp 143–145 °C). Anal. Calcd for $C_{11}H_{13}O_4N_4Cl$: N, 18.63. Found: N, 18.69. The conversion of **9** to chloro olefin **10** was performed 10 times, and low yields were always obtained.[53] The best preparation is described. Under nitrogen, in carefully dried glassware, sodium hydride (50% in wax, 1.3 g (54 mmol) of NaH) was warmed in dry Me_2SO (35 mL) until hydrogen evolution ceased. Freshly prepared methyltriphenylphosphonium bromide (mp 228–231 °C, dried in an oven at 120 °C overnight, 18.92 g, 53 mmol), previously dissolved in hot Me_2SO (50 mL) and then cooled, was added with stirring in one portion to the dimsyl sodium at 15 °C. The dark golden ylide formed. After further stirring for 15 min at 25 °C, aldehyde **9** (6.42 g, 53 mmol) in dry Me_2SO (10 mL) was added in a stream. The solution turned red as the temperature rose to 58 °C. After 2 h the solution cooled to 25 °C. Bulb-to-bulb distillation (100 °C, 120 mm) afforded a distillate, which was taken up in ether (20 mL) and washed with water (30 mL). Removal of the ether from the dried ($MgSO_4$) material left **4-chloro-3,3-dimethyl-1-butene (10)**, which was distilled: bp 108–109 °C (atm), 1.86 g (30%); NMR δ (CCl_4) 5.83, 5.12, 4.90 (m, 3 H, CH=CH₂, ABX, J_{trans} = 18 Hz, J_{cis} = 9 Hz, J_{gem} = 3 Hz), 3.30 (s, 2 H, CH₂Cl), 1.10 (s, 6 H, CH₃); IR (neat) 3110, 1642, 928 (CH=CH₂), 1382, 1368 (CH₃) cm⁻¹. Anal. Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35. Found: C, 61.08; H, 9.50. Other similar preparations or variations using methyltriphenylphosphonium tosylate[54] or n-butyllithium in ether as the base were less effective (0–24% yields). Under nitrogen a neat mixture of olefin **10** (1.59 g, 13.4 mmol) and (chloromethyl)dimethylsilane[55] (2.96 g, 27.3 mmol) was treated with a few drops of chloroplatinic acid hexahydrate in ethanol (0.1 M). The clear solution clouded, effervesced, and within 5 min suddenly turned black and got quite warm (ice-cooling used). When no further reaction was apparent, the solution was held at 65–75 °C for 1.25 h. Bulb-to-bulb distillation (80 °C, 0.3 mm) produced slightly crude **11** (2.16 g, 71%). Purification of **11** by GC (DC-200 column, 150 °C) gave the product as a colorless oil: NMR δ (CCl_4) 3.33 (s, 2 H, CCH₂Cl), 2.73 (s, 2 H, SiCH₂Cl), 1.53–1.17 (m, 2 H, SiCH₂CH₂C), 0.97 (s, 6 H, CCH₃), 0.70–0.30 (m, 2 H, SiCH₂CH₂C), 0.13 (s, 6 H, SiCH₃); IR (neat) 1390, 1370 (C–CH₃), 1260 (Si–CH₃) cm⁻¹. Anal. Calcd for $C_9H_{20}Cl_2Si$: C, 47.57; H, 8.87. Found: C, 47.83; H, 8.89.

6-Chloro-2,2,5,5-tetramethyl-2-silahexane (12). Under a condenser and in a nitrogen atmosphere, olefin **10** (1.67 g, 14 mmol) containing chloroplatinic acid hexahydrate in ethanol (0.12 M, 2 drops) was held at 65 °C as dimethylchlorosilane (Silar Laboratories, 4 g, 42 mmol) was added in portions. The mixture refluxed vigorously. After the addition was completed, further chloroplatinic acid (2 drops) was added, and the solution was allowed to reflux for 45 min. The excess chlorosilane was removed by distillation and the dark residual oil was distilled in a bulb-to-bulb apparatus (100 °C, 5 mm). To the distillate so obtained was added dry ether (10 mL), followed by injection of methyllithium (Foote, 5% in ether, 9 mL) under nitrogen by syringe through a septum, maintaining the temperature at 0 °C. When the vigorous reaction subsided, the mixture was allowed to stand at 25 °C for 15 min. Water was then carefully added, followed by hydrochloric acid (10%, 10 mL). Separation and drying (Na_2SO_4) of the ether phase, followed by evaporation of the solvent, left slightly crude **12** (0.56 g, 21% overall yield). Purification was effected by GC (DC-200 column, 150 °C), affording **12** as a colorless oil: NMR δ (CCl_4) 3.30 (s, 2 H, CH₂Cl), 1.50–1.17 (m, 2 H, SiCH₂CH₂C), 1.0 (s, 6 H, CCH₃), 0.67–0.23 (m, 2 H, SiCH₂CH₂C), 0.07 (s, 9 H, SiCH₃); IR (neat) 1383, 1367 (C–CH₃), 1252, 870–840 (Si–CH₃) cm⁻¹. Anal. Calcd for $C_9H_{21}ClSi$: C, 56.06; H, 10.98. Found: C, 55.72; H, 10.96.

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(52) Kirmse, W.; Schladetsch, H. J.; Bücking, H.-W. *Chem. Ber.* **1966**, *99*, 2579. We thank Counde O-Yang for this preparation.

(53) The poor results obtained in the Wittig conversion of **9** to **10** were a consequence of elimination from the betaine intermediate. Isobutylene was the major product. Similarly, 1,1-diphenylethene was the major product from the tetraphenyl analogue of **9**: Wilt, J. W.; Zieske, P. A., unpublished work. Such poor results have precedent. Only 5% of the expected Wittig product was obtained from 3-chloropropiophenone and methylenetriphenylphosphorane (Pasto, D. J.; Garves, K.; Sevenair, J. P. *J. Org. Chem.* **1968**, *33*, 2975).

(54) Klamann, D.; Weyerstahl, P. *Angew. Chem.* **1963**, *75*, 89.

(55) This silane was more conveniently prepared by treatment of **19** with LiAlH₄. Its properties agreed with those reported by: Seyferth, D.; Rochow, E. G. *J. Am. Chem. Soc.* **1955**, *77*, 907, for this silane made by a different route.

1-Chloro-2,2,5,5-tetramethyl-2-silahexane (13). Neohexene (Aldrich, 2.1 g, 25 mmol) was heated under reflux in the presence of chloroplatinic acid hexahydrate in ethanol (0.12 M, 2 drops). (Chloromethyl)dimethylsilane[55] (3 g, 27.6 mmol) was added dropwise to this mixture, which darkened. Upon completion of the addition, the solution was held at a bath temperature of 160 °C for 2 h, cooled, and diluted with ether (25 mL). The ether material was washed with sodium bicarbonate (5%), water, and brine. The ether was stripped off and the residual oil was distilled bulb to bulb (115 °C, 20 mm) to produce **13** as a colorless oil (3.81 g, 79%). The analytical sample was collected by GC (DC-200 column, 150 °C): NMR δ (CCl_4) 2.73 (s, 2 H, CH₂Cl), 1.40–1.03 (m, 2 H, SiCH₂CH₂), 0.90 (s, 9 H, CCH₃), 0.77–0.32 (m, 2 H, SiCH₂CH₂), 0.12 (s, 6 H, SiCH₃); IR (neat) 1392, 1362 (C–CH₃), 1252 (Si–CH₃). Anal. Calcd for $C_9H_{21}ClSi$: C, 56.06; H, 10.98. Found: C, 55.67; H, 10.74. Isomers **12** and **13** were not resolved upon GC investigation with either DC-200 or Carbowax 20 M columns. However, either isomer can be detected easily at levels of 5% (bw) in the other by NMR analysis.

(1-Chloropropyl)trimethylsilane (15). Ethyl trimethylsilyl ketone (**17**) was prepared by the method of Sakurai and co-workers[11] (86%, spectra in agreement with those reported[12]). To a solution of sodium borohydride (Alfa, 0.28 g, 7.4 mmol) in 95% ethanol (10 mL) was added dropwise with stirring at 25 °C a solution of ketone **17** (3.0 g, 23.1 mmol) in 95% ethanol (5 mL). After the addition the mixture was refluxed for 10 min and cooled. Water (30 mL) followed by petroleum ether (40 mL) was added with stirring. The layers were separated, and the aqueous phase was extracted with petroleum ether (2 × 25 mL). The combined organic material was dried ($MgSO_4$), and the solvent was removed to leave **(1-hydroxypropyl)trimethylsilane (18)** as a colorless oil (2.61 g, 86%). The analytical sample was collected by GC (SE-30 column, 115 °C): NMR δ (CCl_4) 3.17 (dd, 1 H, CHOH, J = 6.3 and 7.9 Hz), 2.03 (s, 1 H, OH), 1.57 (m, 2 H, AB, CH₂), 1.07 (distorted t, 3 H, CCH₃), 0.07 (s, 9 H, SiCH₃); IR (neat) 3400 (OH), 240, 840, 750 (SiCH₃) cm⁻¹. Anal. Calcd for $C_6H_{16}OSi$: C, 54.48; H, 12.19. Found: C, 54.51; H, 12.16.

To alcohol **18** (075 g, 5.8 mmol) in dry ether (5 mL) was added dropwise with stirring at 0 °C a solution of thionyl chloride (0.76 g, 6.4 mmol) in dry ether (5 mL). After the addition the solution was stirred at 0 °C for 20 min. and at 25 °C for another 20 min. and then refluxed for 1 h. Evaporation produced a light brown oil (0.68 g, 78%) that was slightly crude **15**. Purification via GC (SE-30 column, 85 °C) produced the chloride as a colorless oil: NMR δ (CCl_4) 3.05 (dd, 1 H, CHCl, J = 9.5 and 4.8 Hz), 2.00–1.50 (m, 2 H, AB, CH₂), 1.10 (distorted t, 3 H, CCH₃), 0.08 (s, 9 H, SiCH₃); IR (neat) 1250, 840 (SiCH₃) cm⁻¹. Anal. Calcd for $C_6H_{15}ClSi$: C, 47.81; H, 10.03. Found: C, 47.70; H, 9.68.

(2-Chloroethyl)(chloromethyl)dimethylsilane (33). Mercuric acetate (Aldrich, 12.76 g, 40 mmol) was dissolved in water (40 mL), and tetrahydrofuran (THF, 40 mL) was added. To this yellow solution at 25 °C, (chloromethyl)dimethylvinylsilane (Petrarch Systems, 24, 5.0 g, 37 mmol) was added with stirring. The solution decolorized in 30 s, after which stirring was continued for 5 min. Aqueous sodium hydroxide (3 M, 40 mL) was then added, followed by a solution (40 mL) of sodium borohydride (0.5 M) in sodium hydroxide (3 M). Ether (160 mL) was next added to the black solution (suspended mercury), and stirring was continued for 1 h. The solution was saturated with sodium chloride and the THF–ether phase was separated, washed with brine, dried (Na_2SO_4), and freed of solvent. Distillation of the residual oil (Hickman still, bath 80 °C, 0.6 mm) afforded **(2-hydroxyethyl)(chloromethyl)dimethylsilane (32, 3.16 g, 56%)**: NMR δ (CCl_4) 3.69 (t, 2 H, J = 7.9 Hz, CH₂OH), 3.08 (broad s, 1 H, OH), 2.72 (s, 2 H, CH₂Cl), 1.00 (t, 2 H, SiCH₂), 0.14 (s, 6 H, CH₃); IR (neat) 3385 (OH), 1255, 805 (Si–CH₃) cm⁻¹. Anal. Calcd for $C_5H_{13}OClSi$: C, 39.33; H, 8.58. Found: C, 38.98; H, 8.39. No evidence was found for the α-hydroxy isomer of **32**.[56]

To alcohol **32** (3.16 g, 20.8 mmol) dissolved in dry ether (40 mL) and pyridine (0.82 g, 10.4 mmol) at 0 °C was added dropwise with stirring a solution of thionyl chloride (2.48 g, 20.8 mmol) in dry ether (15 mL). The solution was stirred as it warmed to 25 °C and then for an additional day. The material was refluxed for 1 h, cooled, and filtered. The pyridinium chloride precipitate was washed thrice with ether, and the washes were combined with the filtrate. Evaporation of the solvent left crude **33** as a fuming brown oil (2.72 g, 76%). Colorless reaction and analytical material were collected by GC (SE-30 column, 115 °C):
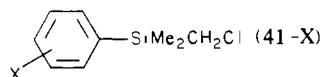
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(56) Electrophilic addition via oxymercuration–demercuration of vinylsilanes is highly regioselective.[57] Such a difference reflects the well-known "β effect"[58] in organosilicon chemistry.

(57) Soderquist, J. A.; Thompson, K. L. *J. Organomet. Chem.* **1978**, *159*, 237.

(58) Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 15–20.

Table XII. Characterization Data for New Aryldimethyl(chloromethyl)silanes

| | | δ (CCl$_4$) | | anal. | | | |
| | | | | carbon | | hydrogen | |
X	bp, °C (mm)	Me	CH$_2$Cl	calcd	found	calcd	found
p-t-Bu^a	123–124 (2)	0.38	2.85	64.83	64.70	8.79	8.73
m-F^b	82–83 (1.5)	0.40	2.85	53.32	53.38	5.97	5.95
p-CF$_3$^{c}	71–72 (0.80)	0.46	2.88	47.52	47.52	4.79	4.78

^{a} Solidifies ~20 °C, δ (t-Bu) 1.32 s. ^{b} 17% yield. ^{c} 14% yield.

NMR (CCl$_4$) 3.61 (t, 2 H, J = 7.9 Hz, CH$_2$CH$_2$Cl), 2.72 (s, 2 H, SiCH$_2$Cl), 1.29 (t, 2 H, CH$_2$CH$_2$Cl), 0.16 (s, 6 H, CH$_3$); IR (neat) 1290 (CH$_2$Cl), 1250, 850 (Si–CH$_3$) cm^{-1}. Anal. Calcd for C$_5$H$_{12}$Cl$_2$Si: C, 35.09; H, 7.07. Found: C, 34.84; H, 7.05.

(α-Chlorobenzyl)triethylsilane (26). (Benzyloxy)triethylsilane (38) was prepared in ether (72 h, 25 °C) from benzyl alcohol and triethylchlorosilane (Petrarch Systems) in the presence of pyridine [91%, bp 140 °C (10 mm), lit.[28] bp 162 °C (20 mm)]. The rearrangement of 38 to (±)-(α-hydroxybenzyl)triethylsilane (39) was performed according to the procedure of West et al.[28] The increased scale of the present preparation warrants a detailed description. Under nitrogen, ether 38 (57.27 g, 303 mmol) in dry pentane (100 mL) was treated dropwise at 25 °C via syringe with *tert*-butyllithium in pentane (Aldrich, 2 M, 159 mL, 318 mmol). The now yellow solution was *mechanically* stirred at room temperature for 216 h, over which time a brown color developed. Hydrochloric acid (20%, 600 mL) was then added cautiously. The layers were separated and the solvent was stripped from the organic phase to leave a yellow oil (69.63 g). NMR analysis showed that this oil contained alcohol 39 (38 g) with the remainder being mostly ether 38.[59] The two could not be separated by distillation in a 35-plate column. Other reactant ratios and/or reaction times gave less favorable conversions on this scale.

The above oil (69.63 g), phthalic anhydride (46.51 g, 314 mmol), and pyridine (45.97 g, 47 mL, 581 mmol) were heated on a steam bath for 3 h. While still warm, the mixture was poured onto ice (157 g) and concentrated hydrochloric acid (55 mL). The aqueous layer, decanted when the ice melted, was extracted with chloroform (3 × 10 mL). The organic material was combined with these chloroform extracts and rotary evaporated to leave a brown oil. The oil was dissolved in aqueous sodium bicarbonate (34.94 g in 364 mL of water) and the upper organic layer was saved for reisolation of unchanged ether 38. The alkaline layer was extracted with ether (4 × 100 mL) and the extracts were combined with the organic layer mentioned above. Acidification of the aqueous material with hydrochloric acid (10%, litmus paper detection) formed two layers. The entire material was shaken with chloroform (3 × 100 mL), and the chloroform extracts were combined and stripped. The oil remaining was added to a hot solution of glacial acetic acid and the water (200 mL, v/v = 85:15, respectively). Upon cooling, the racemic hydrogen phthalate ester of 39 crystallized from solution as white crystals that were washed with cold water (100 mL) and dried in air (37.73 g, 60%, mp 130–131 °C): NMR δ (CDCl$_3$) 10.55 (broad s, 1 H, COOH), 8.16–7.13 (m, 9 H, Ar H), 6.10 (s, 1 H, CHO), 1.18–0.33 (m, 15 H, CH$_2$CH$_3$); IR (KBr) 3040 (OH), 1700 (C=O), 1250, 1000, 925 (Si–CH$_2$CH$_3$) cm^{-1}. Anal. Calcd for C$_{21}$H$_{26}$O$_4$Si: C, 68.07; H, 7.07. Found: C, 68.04; H, 6.96.

Resolution was accomplished by treating the racemic hydrogen phthalate ester (32.87 g, 88.7 mmol) with (−)-strychnine (Aldrich, 29.71 g, 88.8 mmol) in chloroform (140 mL).[60] The mixture was heated on a steam bath until the solid ester dissolved. The solution was cooled and evaporated, to leave a clear viscous oil. Sequential treatment of this material with hot (70 °C) ethyl acetate caused the less soluble (−) diastereoisomer to precipitate as a white crystalline solid (most at 25 °C, some in the freezer after 3 h). The more soluble (+) diastereoisomer was obtained by removal of the solvent as a white foam-like solid. After three such treatments on these solids, satisfactory resolution of these 39 hydrogen phthalate strychnine salts was achieved: less soluble diastereoisomer, mp 208–210 °C, [α]^{27}$_D$ −42.7° (CHCl$_3$, c 0.0281 g/mL), 27.13 g, 75% recovery; more soluble diastereoisomer, mp 70–78°C, [α]^{30}$_D$

+21.5° (CHCl$_3$, c 0.0557 g/mL), 7.73 g, 21% recovery. The (−) isomer was analyzed. Calcd for C$_{42}$H$_{48}$N$_2$O$_6$Si·^{1}/$_2$H$_2$O: C, 70.66; H, 6.92. Found: C, 70.55; H, 6.91.

A sample conversion of these salts back to the esters is described. The (−) diastereoisomer (27.13 g, 38 mmol) was dissolved in warm absolute ethanol (300 ml). When cool, the solution was treated with hydrochloric acid (10%, 600 mL). The (−)-hydrogen phthalate ester precipitated as a white solid. The entire mixture was extracted with ether (3 × 100 mL); the extracts were combined, washed with water (3 × 100 mL) and brine, and dried (Na$_2$SO$_4$). Removal of the ether left the ester as a crystalline solid (13.3 g). The aqueous material was saved to recover the strychnine.[61] In this fashion was obtained the (−)-hydrogen phthalate ester of 39 [mp 108–110 °C, [α]^{30}$_D$ −69.2° (CHCl$_3$, c 0.0347 g/mL), 93%] and the (+) enantiomer [mp 112–114 °C, [α]^{30}$_D$ +79.3° (CHCl$_3$, c 0.0492 g/mL), ~100%].

Hydrolysis of the active hydrogen phthalate esters to their active alcohols 39 was frustrating. Use of aqueous or alcoholic sodium hydroxide at various temperatures invariably led to cleavage products, benzyl alcohol, triethylsilanol, and ether 38.[62] Ester interchange with hot methanol was ineffectual. Treatment with lithium aluminum hydride led to nondescript complex mixtures. Use of hydrazine or liquid ammonia simply formed salts. Acid hydrolysis was ill-advised due to potential racemization problems. Cleavage using Grignard or organolithium reagents was more promising,[64] but the phthalide byproducts were troublesome. Eventually "hydrolysis" was achieved as described for a representative case. Under nitrogen, magnesium (37.22 g, 1.53 mol) in dry ether (250 mL) was treated dropwise *at reflux* with a mixture of *p*-bromo-*N,N*-dimethylaniline (141.76 g, 0.709 mol) and ethylene bromide (154.6 g, 0.822 mol) in dry ether (400 mL).[65] The solution was refluxed for 45 min after the addition and cooled. The (−)-hydrogen phthalate ester of 39 (12.78 g, 35.5 mmol) in dry ether (100 mL) was then added dropwise and the solution was stirred for 2 h. Saturated ammonium chloride solution (750 mL) was added slowly at 0 °C, followed by water (100 mL). The entire material was filtered through a cotton pad, and the layers were separated. The aqueous phase was extracted with ether (3 × 100 mL) and the extracts combined with the organic phase. This material was extracted with hydrochloric acid (10%, 8 × 200 mL), water (3 × 200 mL) and brine and dried (Na$_2$SO$_4$). Removal of the solvent left (−) alcohol 39 as a pale yellow oil (7.52 g, 98%). In this way was obtained (−)-39, [α]^{26}$_D$ −70.4° (CHCl$_3$, c 0.0398 g/mL), and (+)-39, [α]^{26}$_D$ +81.8° (CHCl$_3$, c 0.0477 g/ml): NMR δ (CDCl$_3$) 7.25 (s, 5 H, Ar H), 4.63 (s, 1 H, CHOH), 1.72 (s, 1 H, OH), 1.31–0.30 (m, 15 H, CH$_2$CH$_3$); IR (neat) 3450 (OH), 1236, 1006 (Si–CH$_2$CH$_3$) cm^{-1}. Alcohol 39 is air sensitive, soon developing a benzaldehyde odor and darkening on standing. The active alcohols were therefore quickly converted to chloride 26.

Samples of alcohol 39 differing in optical purity were converted to 26. A representative preparation is given. Under nitrogen, a sample of active alcohol (−)-39 ([α]^{26}$_D$ −70.4°, 2.0 g, 9 mmol) in dry pentane (90 mL) was treated dropwise with stirring at 25 °C with a solution of thionyl chloride (4.28 g, 36 mmol) in dry pentane (40 mL). Reaction was allowed to continue for 17.5 h. Water (95 mL) was then added, and the solution was stirred until gas evolution ceased. The layers were separated

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(59) On a smaller scale (22.4 mmol of 38) West and co-workers[28] obtained 75% rearranged 39 in 48 h. Use of excess *t*-BuLi for a longer time increased the rearrangement even further. For our purposes the present procedure was adequate, particularly because unchanged 38 could be recovered.

(60) A number of other alkaloids and solvents were tried but this combination was the only successful one.

(61) Details such as this may be found in the dissertation of F.G.B.

(62) It is conjectured that saponification afforded 39 that then underwent a Brook[63] rearrangement to 38 and was subsequently partially cleaved by base to the benzyl alcohol and silanol.

(63) Brook, A. G. *Pure Appl. Chem.* 1966, 13, 215.

(64) Our view is that 39 must be kept throughout the cleavage as the alkoxide in a strongly basic environment in order to prevent problems as in ref 62.

(65) Pearson, D. E.; Cowan, D.; Beckler, J. D. *J. Org. Chem.* 1959, 24, 504.

Table XIII. Characterization Data for Aryldimethyltin Compounds

X	compd	yield, %	bp, °C (mm), [mp]	¹H NMR, δ[a]			
				Ar H	Sn–H[b]	Sn–Me[c]	X
H	A[d]	79	96–98 (0.1)	7.5–7.2 m		0.48 s	
	B[d]	52	100–101 (1.4) [25–26]	7.6–7.3 m		0.77 s	
	C	52		7.6–7.2 m	5.47 m	0.25 d	
CH₃	A[d]	68	110–112 (0.1)	7.4–7.0 m		0.44 s	2.27 s
	B	40	[24–26]	7.4–7.0 m		0.97 s	2.34 s
	C	58		7.6–7.3 m	5.47 m	0.28 d	2.23 s
OCH₃	A	70	[28–30]	7.4–6.8 m		0.44 s	3.74 s
	B	53	[28–30]	7.6–6.5 m		0.99 s	3.74 s
	C	48		7.5–6.3 m	5.43 m	0.23 d	3.19 s
F	A[e]	65	88–92 (0.1)	7.5–6.9 m		0.49 s	
	B	65	65–70 (0.1) [25–27]	7.6–7.0 m		0.79 s	
	C	38		7.3–6.7 m	5.39 m	0.15 d	
CF₃	A	80	98–101 (0.1)	7.61 s		0.59 s	
	B	69	86–89 (0.1) [48–50]	7.63 s		0.85 s	
	C	50		7.5–7.2 m	5.37 m	0.18 d	

[a] For A and B spectra were determined in CCl₄ containing Me₄Si; for C in benzene-d_6 containing dimethyl carbonate (δ 3.33).   [b] Septet, $J \cong 1$ Hz.   [c] Sidebands due to $J(^{119}Sn) = 53–61$ Hz were seen in all cases. In C $J_{vic} = 2.5–3$ Hz.   [d] Reference 71.   [e] Angelletti, J. M.; Maire, J. C. *Bull. Soc. Chim. Fr.* 1959, 1858.

Table XIV. Ultraviolet Spectral Data

compd	concn, M	λ_max^isooctane, nm	ε (at λ)		
			max	254	300
TBTH	4.7 × 10⁻³	217	532	19	6
	0.8	248 br	4.4	4.4	0.088
1	4.7 × 10⁻³	203	283	0	0
	0.92	224, 262	3.6, 3.2	2.8	0.3

and the aqueous phase was extracted with petroleum ether (3 × 50 mL). The combined organic material was washed with water (2 × 50 mL), sodium bicarbonate solution (5%, 2 × 50 mL), water and brine and dried (Na₂SO₄). Removal of the solvent afforded (−)-**26** [2.16 g, ~100%, $[\alpha]^{27}_D$ −71.9° (CHCl₃, c 0.0334 g/mL)] as a pale yellow oil. Analogous treatment gave (+)-**26** [87%, $[\alpha]^{22}_D$ +89.3° (CHCl₃, c 0.0129 g/mL)]. The latter was distilled (Hickman still, bath 110 °C, 0.3 mm) to give a colorless oil: NMR δ (CCl₄) 7.18 (s, 5 H, Ar H), 4.36 (s, 1 H, CHCl), 1.35–0.46 (m, 15 H, CH₂CH₃); IR (neat) 1244, 1014 (Si–CH₂CH₃) cm⁻¹. Anal. Calcd for C₁₃H₂₁ClSi: C, 64.83; H, 8.79. Found: C, 65.05; H, 8.78.

Aryldimethyl(chloromethyl)silanes ("Sila-Neophyl Chlorides", 41-X). This group of compounds was prepared in variable yield (14–55%) by the reported method from the corresponding aryl Grignard reagent and chlorosilane **19**.[66] Known chlorides synthesized were **41**, X = H,[66] m-CH₃,[67] m-CF₃,[68] p-F,[68] p-OCH₃,[69] p-Cl,[69] and p-CH₃.[69] Data for new compounds are given in Table XII.

Aryldimethyltin Hydrides (42-X). All of the compounds in this series presented problems in combustion microanalysis, not an unexpected occurrence in organotin chemistry.[70] Their structures are supported by spectra only. Their purity was assayed as mentioned (vide infra). **Diaryldimethyltins** were prepared as reported,[71] as were the **aryldimethyltin iodides** formed from them by cleavage with iodine.[72] Titration of these iodides with standardized silver nitrate indicated purities of ca. 95%. Reduction of the iodides to the **aryldimethyltin hydrides 42**-X with lithium aluminum hydride in ether was modeled upon the analogous reduction of tri-n-butyltin hydride.[44] Gasometric analysis of **42**-X with hydro-

chloric acid (10%) showed purities of ca. 90%. Data for all these compounds are collected in Table XIII.

Lanthanide and Chiral Solvent Shift Studies.[73] Use of the chiral shift reagent Eu(hfc)₃ (Aldrich) with samples of active alcohol **39** in the usual way indicated that the pure enantiomers would have $[\alpha]_D$ values of (+) or (−) 92.6–96°. Employing the chiral solvents (+)- or (−)-2,2,2-trifluoro-1-(9-anthryl)ethanol (Aldrich) led to the value of (+) or (−) 105.2° for the pure enantiomers. Depending upon which of these values is chosen, the three recrystallizations described earlier (vide supra) led to 64–76% and 75–88% ee for the (−) and (+) enantiomers, respectively, of alcohol **39**. Unfortunately, the chiral solvents (in CCl₄) did not resolve the resonances of chloride **26**. Use of the bridging pair Ag(fod)–Eu(or Pr)(hfc)₃[74] on **26** or the silanes **40** was inconclusive.

Competitive Reductions. Reactions were performed under nitrogen (unless stated otherwise) on a 0.5–1.0 mmol scale. Reactions were followed by NMR or GC analysis until no further change in composition was observed (2–6 h). Equation 27 was used in most of these studies,[8]

$$k_A/k_B = \frac{\ln ([A]_0/[A]_t)}{\ln ([B]_0/[B]_t)} \qquad (27)$$

where the concentrations were measured either as *integration ratios* (error ±10%) of certain NMR signals (normally the CH₂Cl or CHCl resonance, relative to an internal standard, trioxane, diphenylmethane, or dimethyl carbonate in benzene or isooctane solvent) or analogously as *peak areas* (cut and weigh method) in GC (error ±5%), relative to an internal standard (decane or 2,4-dimethylpentane) in decalin solvent. At times sequential comparisons were made between two reactants of comparable reactivity and thence indirectly to **1**. Such cases are mentioned in the tables. In those reductions of **1** using **42**-X or TPTH and TPGH,[75]

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(75) We are indebted to Undergraduate Research Scholar Carrie Kwasigroch for the studies on TPTH, TPGH, and triphenylsilane.

individual k_T values were determined at 366 nm by NMR and compared to the standard reductant in each case, as described in the text. Isooctane was the solvent for the studies with **42-X**, deuteriobenzene for TBTH and TPGH.

In a number of reductions, the solvent was removed and the products were collected by GC. In every case the expected product (C-X → C-H) was found. The yields were >90%.

Ultraviolet spectral data are collected in Table XIV. The data indicate that TBTH is the more likely initiator, rather than **1**, in those reductions not containing AIBN or DTBP.

Generation and Chemical Properties of Dicyclopropylcarbene. Ring Expansion, Chlorine Abstraction, C–H Insertion, and Alkene Addition Reactions

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1. Received November 5, 1982. Revised Manuscript Received May 9, 1983

Abstract: Thermolysis of 5,5-dicyclopropyl-2-methoxy-2-methyl-Δ³-1,3,4-oxadiazoline in solution at 80 °C affords dicyclopropylcarbene and methyl acetate in high yields. Dicyclopropylcarbene undergoes a variety of reactions including ring expansion to 1-cyclopropylcyclobutene, chlorine atom abstraction from carbon tetrachloride, and efficient insertion into the CH bond of chloroform. A rationale for the very different reactions of the carbene with CCl₄ and CHCl₃ is suggested. Carbene trapping by addition to tetrachloroethylene, using the oxadiazoline as the carbene source, is illustrated with the preparation of an adduct.

Recently we reported[1,2] the thermal generation of carbenes by thermolysis of 2-substituted 2,5,5-trialkyl-Δ³-1,3,4-oxadiazolines (**1–3**) (eq 1). The carbenes are formed from a short-lived

$$ \text{(1)} $$

1–5

6
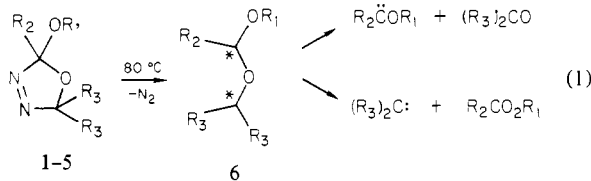
1, R₁ = R₂ = R₃ = CH₃
2, R₁ = COCH₃; R₂ = CH₃; R₃ = *c*-C₃H₅
3, R₁ = COCH₃; R₂ = CH₂CH₃; R₃ = *c*-C₃H₅
4, R₁ = R₂ = CH₃; R₃ = *c*-C₃H₅
5, R₁ = H; R₂ = CH₃; R₃ = *c*-C₃H₅

carbonyl ylide precursor (**6**) that can be trapped with methanol[1] or with dipolarophiles.[3] Fragmentation of the ylide **6** is not very selective in the case of **1–3**, which detracts from the synthetic utility of the oxadiazolines as carbene precursors.

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As part of a search for oxadiazolines that fragment to only one of two possible carbenes, we synthesized **4**, and we now report that its thermolysis in solution affords dicyclopropylcarbene in about 80% yield. Some intramolecular and intermolecular reactions of that carbene are also reported.

Experimental Section

Dicyclopropyl Ketone *N*-Acetylhydrazone. A solution of dicyclopropyl ketone (11.0 g, 0.100 mol) and acetylhydrazine (7.4 g, 0.10 mol) in 95% ethanol (100 mL) containing acetic acid (2 mL) was refluxed for 30 min. Most of the solvent was distilled off, and the residue was heated at 120 °C for 3 h. The residue, which solidified on cooling, was recrystallized from acetone to give material melting at 114–115 °C in 90% yield: ¹H NMR (CDCl₃) δ 0.50–1.01 (m, 8 H), 1.13–1.60 (m, 2 H), 2.20 (s, 3 H). Anal. Calcd for C₉H₁₄NO: C, 65.03; H, 8.50; N, 16.85. Found: C, 65.00; H, 8.39; N, 16.98.

5,5-Dicyclopropyl-2-methoxy-2-methyl-Δ³-1,3,4-oxadiazoline (4). To lead tetraacetate (4.44 g, 0.010 mol) in ice-cold absolute methanol was added, with stirring, dicyclopropyl ketone–*N*-acetylhydrazone (1.66 g, 0.010 mol). When the initial yellow color of the solution had faded, KOH (pellets, 2 g) was added to hydrolyze the 5,5-dicyclopropyl-2-acetoxy-2-methyl-Δ³-1,3,4-oxadiazoline (**2**), which is a coproduct of the oxidation. Stirring and cooling were maintained for 2 h after which most of the methanol was removed with a rotary evaporator. Water and methylene chloride were added to the residue and the organic layer was separated. It was washed with water and dried over calcium chloride before the solvent was evaporated to afford **4** in 71% yield as an oil that