J. Org. Chem. 1992, 57, 3405-3409

# The $Me_3Si$ Substituent Effect on the Reactivity of Silanes. Structural Correlations between Silyl Radicals and Their Parent Silanes

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*Received December 26, 1991*

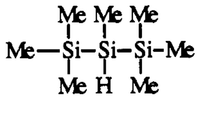
Good linear correlations exist both between the bond dissociation energy of an Si–H bond and the corresponding SiH stretching frequency and between the $^{29}Si$ hyperfine splitting of a silicon-centered radical and $J(^{29}\mathrm{Si{-}H})$ for the corresponding silane, when the successive substitution at the Si–H function takes place inside a family, i.e., $(Me_3Si)_{3-n}Si(H)Me_n$, $n = 0{-}3$. Explanations for these phenomena are advanced. Such structural correlations allow the characterization of $(Me_3Si)_2Si(H)Me$ as a radical-based reducing agent with low hydrogen-donating abilities. Rate constants for the reaction of primary alkyl radicals with $(Me_3Si)_2Si(H)Me$ have been measured over a range of temperatures by using competing unimolecular radical reactions as timing devices. The radical trapping abilities of this silane and other common radical-based reducing agents are compared.

## Introduction

The majority of radical reactions of interest to synthetic chemists are chain processes. Probably the best known and most useful free-radical reactions are the reductions of organic substrates by tributyltin hydride[1] (cf. Scheme I). In recent years, tris(trimethylsilyl)silane as an alternative to $Bu_3SnH$ has become more and more popular,[2] being a superior reagent from both ecological and practical perspectives.

For the design of new radical reactions, one is faced with the difficult task of selecting the reducing agent and particular experimental conditions depending upon the abilities of hydrogen donation of hydrides. For example, the rapidity of hydrogen transfer (cf. Scheme I) is not an advantage when the synthetic strategy requires another radical reaction to take place before the hydrogen-transfer step.[3] Therefore, the slowness may be a desirable characteristic given the limitation that the reaction must proceed with reasonable chain length to give decent yields. Since $Bu_3SnH$ has been for many years the only radical-based reducing agent, some practical methodologies have been developed to compensate for the lack of compounds with different hydrogen abilities. Thus, the syringe-pump method[4] or $Bu_3SnX/NaBH_4$ systems[5] have been used to keep tin hydride at low concentration during the reaction time. However, all these methods have their weaknesses. It has been suggested that tributylgermanium hydride is a suitable reagent for this purpose,[6] although high cost makes its use unattractive.

As we already mentioned, the silicon–hydrogen bond strength in organosilanes can be modulated by the substituents, and therefore a wide range of hydrogen-donor abilities is possible.[2] In the present work, we have extended the use of 1,1,1,2,3,3,3-heptamethyltrisilane (1) as radical reducing agent.



$$\mathrm{Me{-}\underset{Me}{\overset{Me}{Si}}{-}\underset{H}{\overset{Me}{Si}}{-}\underset{Me}{\overset{Me}{Si}}{-}Me}$$

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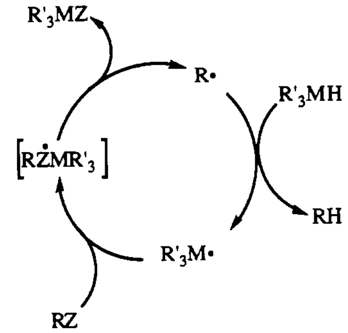
**Scheme I. Propagation Steps for the Reduction Reaction**[a]



[a] $[\mathrm{R\dot{Z}MR'_3}]$ represent a transition state or a reactive intermediate.

## Results and Discussion

**Correlation between BDE and $\nu_{\mathrm{Si{-}H}}$ in $Me_3Si$-Substituted Silanes.** A knowledge of the bond dissociation energies has always been regarded as fundamental to the understanding of chemical bonding and reactivity. In the last decade a number of Si–H bond dissociation energies in organosilanes has been measured and investigation of the specific effects of various substituents has been reported.[7,8] In particular, (i) the successive Me substitution produces no change in Si–H bond strength,[9] (ii) the weakening by Ph substitution is only ca. 8 kJ $mol^{-1}$, the effect being cumulative by further phenyl substitution,[10] and (iii) a profound effect is produced by an adjacent fluorine or $Me_3Si$ group.[11] However, a chemical understanding of the situation is not yet reached.

Figure 1 shows that a correlation exists between BDE(Si–H) and silicon–hydrogen stretching frequency if the variation takes place inside a family.[12] Thus, the Si–H bond strength is not altered by methylation whereas suc-

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[1] Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237 and references cited therein.

[2] Chatgilialoglu, C. *Acc. Chem. Res.*, in press and references cited therein.

[3] In the carbon–carbon bond formation, for example, the alkyl radical attacks alkene intra- or intermolecularly to form the adduct radical prior to reaction with the hydrogen donor.

[4] For an example, see: Porter, N. A.; Lacher, B.; Chang, V. H.; Magnin, D. R. *J. Am. Chem. Soc.* **1989**, *111*, 8309.

[5] For an example, see: Giese, B.; González-Gómez, J. A.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 69.

[6] Lusztyk, J.; Maillard, B.; Deycard, S.; Linday, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509 and references cited therein.

[7] (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; pp 371–391.

[8] Chatgilialoglu, C. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Dordrecht, 1989; pp 115–123.

[9] This is apparently at odds with a model based on correlating isolated vibration frequencies and anharmonicities amongst the methylsilanes (McKean, D. C. *J. Mol. Struct.* **1984**, *113*, 251 and references cited therein).

[10] Lesage, M.; Martinho Simões, J. A.; Griller, D. *J. Org. Chem.* **1990**, *55*, 5413.

[11] Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267.

[12] For a correlation between isolated CH stretching frequencies and bond dissociation energies of CH bonds, see: McKean, D. C. *Int. J. Chem. Kinet.* **1989**, *21*, 445. A correlation between isolated SiH stretching frequencies and ground-state bond lengths over 15 molecules reveals a somewhat reduced sensitivity compared with the corresponding CH correlation (Duncan, J. L.; Harvie, J. L.; McKean, D. C.; Cradock, S. *J. Mol. Struct.* **1986**, *145*, 225).

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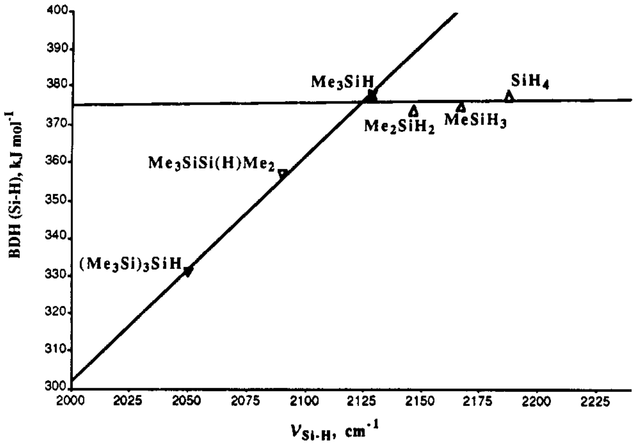
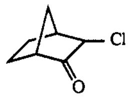
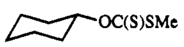
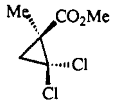
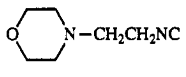
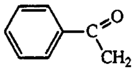
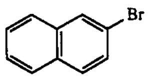


**Figure 1.** Correlation diagram between bond dissociation energies of silanes and the corresponding SiH stretching frequencies.

**Table I. Reduction of Some Organic Compounds by $(Me_3Si)_2Si(H)Me$**

| RX | yield RH[a] (%) | RZ | yield RH[a] (%) |
|---|---|---|---|
|  | 94 |  | 96 |
|  | 93[b] |  | 98 |
| $CH_3(CH_2)_{14}CH_2Br$ | 93 |  | 86 |
|  | 98 |  | 90 |
|  | 90 | $Me_3CCH_2CMe_2NC$ | 75 |
| $CH_3(CH_2)_{14}CH_2I$ | 95 | $Me_3SiCH_2NC$ | 98 |

[a] Yields by GC analysis based on formation of RH. [b] Replace only one chlorine atom.

cessive silyl substitution produces a substiantial Si–H bond weakening effect. It is expected that interactions such as (3d–3p)π bonding or/and hyperconjugation will increase the radical stabilization energy by successive substitution of silyl group at the radical center. We suggest that such interactions together with the inductive effect of the substituents will decrease the BDE(Si–H) and will decrease the $\nu_{Si-H}$. Although this analysis is somewhat speculative as the available thermochemical data allow the construction of only two families, we were led to study the behaviour of $(Me_3Si)_2Si(H)Me$. The latter has a $\nu_{Si-H}$ = 2075 cm$^{-1}$ and we calculated from Figure 1 a BDE(Si–H) = 347 kJ mol$^{-1}$. This estimated value is similar to the BDE of trialkylgermanium hydrides,[13] and therefore, it is expected that $(Me_3Si)_2Si(H)Me$ may be an attractive alternative to $Bu_3GeH$ for a variety of radical chain reactions.

**Reduction of Organic Derivatives.** Reduction of a variety of organic derivatives was carried out by using silane 1. Reactions of each derivative with 1 at 75–90 °C in toluene or benzene and in the presence of a radical initiator, i.e., AIBN, gave the corresponding hydrocarbons in good yields (see Table I). Sample analyses were carried out using GC and authentic samples as calibrants. Yields were quantified by using an internal standard.

**Table II. Kinetic Data for the Reaction of 6-Bromohex-1-ene with $(Me_3Si)_2Si(H)Me$ in *tert*-Butylbenzene at Various Temperatures**

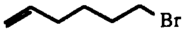
| $T$, K | $[(Me_3Si)_2Si(H)Me]$,[a] M | $k_c/k_H$,[b] M |
|---|---|---|
| 294 | 1.98–3.90 | 7.668 ± 0.331 |
| 313 | 1.21–3.48 | 8.540 ± 0.947 |
| 323 | 1.30–2.62 | 8.681 ± 0.272 |
| 332 | 1.13–3.70 | 9.113 ± 0.573 |
| 353 | 1.31–3.90 | 9.743 ± 0.573 |
| 373 | 1.31–4.00 | 10.206 ± 0.629 |
| 393 | 1.86–3.75 | 11.476 ± 1.436 |

[a] Range of concentration employed. [b] Errors correspond to one standard deviation.

Evidence for a free-radical chain mechanism (cf. Scheme I) was provided by the observations that the reactions were catalyzed by light and by thermal sources of free radicals such as AIBN and dibenzoyl peroxide. Furthermore the reactions were retarded by 2,6-*tert*-butyl-4-methylphenol and duroquinone, which are expected to be inhibitors of the two propagation steps, respectively.

Reductions of bromides and iodides were straightforward, and the reactions were complete after a short time. Secondary alkyl xanthates and selenides were also reduced by the silane, as expected in view of the affinity of silyl radicals for sulfur and selenium-containing substrates. Primary, secondary, and tertiary isocyanides gave the corresponding hydrocarbon in good yields (Table I). For chlorides and sulfides the reductions were difficult due to the shorter chain lengths. Therefore, a longer reaction time and periodic addition of initiator were necessary. However, the reduction of chlorides is facilitated when α-stabilizing groups or in *gem*-dichlorides are present (see Table I).

**Reaction of Primary Alkyl Radicals with $(Me_3Si)_2Si(H)Me$.** An indirect procedure for measuring the rate constant of a radical–molecule reaction involves a competition between this process and a unimolecular path of the radical (free-radical clocks).[14] For example, absolute values of the rate constant for H atom abstraction from a hydride (AH) by an alkyl radical can be obtained, providing that conditions can be found in which an unrearranged radical U• either reacts with AH or rearranges to R• with a known rate constant. By measuring the relative yields of UH and RH at various hydride concentrations, one is able to calculate the rate constant ratio. Bromides 2 and 3 were chosen as precursors of primary alkyl radicals since their unimolecular reactions, under free-radical conditions, have been studied in detail (vide infra).



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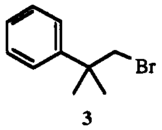

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The 5-hexenyl radical was formed from the corresponding alkenyl bromide 2 and $(Me_3Si)_2Si(H)Me$ by a thermally initiated or photoinitiated radical chain reaction in *tert*-butylbenzene. The two major hydrocarbon products were 1-hexene and methylcyclopentane,[15] the relative

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(13) Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746.

(14) For reviews, see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Essay 4. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(15) Minor quantities of cyclohexane were also formed, its concentration relative to methylcyclopentane increasing with temperature from 1.7% (relative to methylcyclopentane) at 294 K to 3.6% at 393 K (As expected, see: Walling, C.; Cooley, J. H.; Poramas, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361).

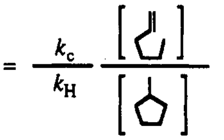
**Table III. Kinetic Parameters for the Reaction of Primary Alkyl Radicals with Silicon, Germanium, and Tin Hydrides**

| hydride | log *A*, $M^{-1}\ s^{-1}$ | $E_a$, kcal $mol^{-1}$ | $k_H^{298}$, $M^{-1}\ s^{-1}$ | ref |
|---|---|---|---|---|
| $(Me_3Si)_2Si(H)Me$ | 8.89 ± 0.39 | 5.98 ± 0.53 | $3.2 \times 10^4$ | this work[a] |
| $n$-$Bu_3GeH$ | 8.44 ± 0.47 | 4.70 ± 0.62 | $9.3 \times 10^4$ | 22[a] |
| $(Me_3Si)_3SiH$ | 8.86 ± 0.68 | 4.47 ± 0.92 | $3.8 \times 10^5$ | 23[a] |
| $n$-$Bu_3SnH$ | 9.07 ± 0.24 | 3.69 ± 0.32 | $2.3 \times 10^6$ | 18[b] |

[a] 5-Hexenyl radical. [b] Combined data for ethyl and *n*-butyl radical.

concentrations of which varied in the expected manner at each temperature as the concentration of silane was changed. If the hydride concentration remains essentially constant under the experimental conditions, then the following relation holds where $k_H$ and $k_c$ are the rate

$$\left[(Me_3Si)_2Si(H)Me\right] =$$



(1)

constants for hydrogen abstraction and the cyclization reaction, respectively. Mean values of the $k_c/k_H$ ratio were obtained at different silane concentrations according to eq 1. The data are summarized in Table II, while the detailed results of the individual experiments are available as supplementary material. Analysis of these data yields the Arrhenius expression

$$\log (k_c/k_H)(M) = (1.53 \pm 0.07) - (0.87 \pm 0.11)/\Theta \quad (2)$$

where $\Theta = 2.3RT$ kcal $mol^{-1}$ and the errors correspond to 95% confidence limits.[16] The absolute value of the rate constants for H atom abstraction from $(Me_3Si)_2Si(H)Me$ by the primary alkyl radical, i.e., $k_H$, can be obtained by combining eq 2 with the Arrhenius equation for the 5-hexenyl cyclization:[17]

$$\log k_H\ (M^{-1}\ s^{-1}) = (8.89 \pm 0.39) - (5.98 \pm 0.53)/\Theta \quad (3)$$

In a similar manner, we measured the rate constant for the reaction of 5-hexenyl radical with $(Me_3Si)_2Si(D)Me$ and found it to be $6.7 \times 10^4\ M^{-1}\ s^{-1}$ at 353 K. Detailed results of this experiment are also available as supplementary material.

In this study, we have also used the neophyl rearrangement[19] as radical clock to investigate the rate constant for the reaction of primary alkyl radicals with $(Me_3Si)_2Si(H)Me$. The neophyl radical was formed from the corresponding bromide 3 and $(Me_3Si)_2Si(H)Me$ by thermally initiated (AIBN) radical-chain reaction in benzene at 348 K. A GC analysis of the reaction mixture showed two products: *tert*-butylbenzene and isobutylbenzene. The kinetic treatment was based on the expected mechanism using the technique described above. A mean value of $k_r/k_H = 0.13$ M was obtained at different silane concentrations. Detailed results of this experiment are also available as supplementary material. By taking $k_r = 1.5 \times 10^4\ s^{-1}$ at 348 K[20] we calculate $k_H = 1.2 \times 10^5\ M^{-1}\ s^{-1}$ which is in good agreement with the value of $k_H = 1.4 \times 10^5\ M^{-1}\ s^{-1}$ obtained from the Arrhenius eq 3.

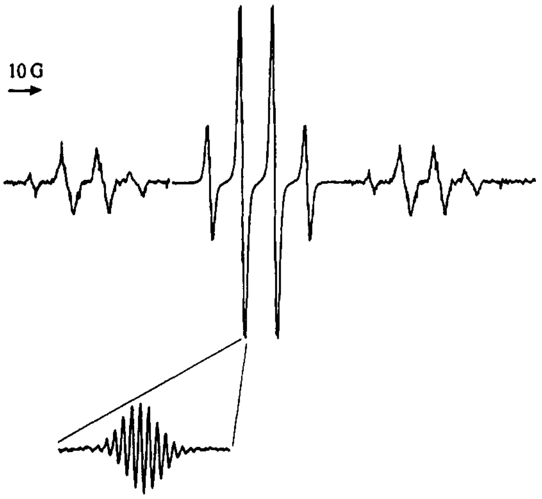


**Figure 2.** ESR spectrum of $(Me_3Si)_2\dot{S}iMe$ recorded at 223 K. The satellite regions were recorded with a 10-fold increase of the gain. The inset shows an enlargement of the second spectral line recorded at lower modulation amplitude revealing hyperfine structure from 18 equivalent protons.

Kinetic parameters for the reaction of primary alkyl radicals with $(Me_3Si)_2Si(H)Me$ are compared in Table III with analogous parameters for their reaction with other group 14 organometallic hydrides. The order of reactivity is $n$-$Bu_3SnH$ > $(Me_3Si)_3SiH$ > $n$-$Bu_3GeH$ > $(Me_3Si)_2Si(H)Me$ with hydrogen-donating ability covering a range of 100. This order follows the difference in bond strength[24] which is manifest above all in enthalpies of activation. The Arrhenius preexponential factors all lie in the expected range. The deuterium kinetic isotope effect for the reaction of primary alkyl radicals with $(Me_3Si)_2Si(H)Me$ is found to be 2.3 (at 353 K) which is in line with the value of 2.3 for $(Me_3Si)_3SiH$[23] and n-$Bu_3SnH$[18] at 363 and 330 K, respectively. The fact that $(Me_3Si)_2Si(H)Me$ is ca. 10 and 100 times less reactive than $(Me_3Si)_3SiH$ and $n$-$Bu_3SnH$, respectively, toward alkyl radical imply that this silane is good for radical-chain reaction in which the desired product must be formed by a *slow* hydrogen transfer.

**Reaction of *tert*-Butoxyl with $(Me_3Si)_2Si(H)Me$.** The relative reactivities of $(Me_3Si)_2Si(H)Me$, $Me_3SiSi(H)Me_2$, and $(Me_3Si)_3SiH$ toward $t$-$BuO^\bullet$ radicals have been obtained by GC analysis followed by the photochemically initiated reaction between di-*tert*-butyl peroxide and either $(Me_3Si)_2Si(H)Me$ and $Me_3SiSi(H)Me_2$ or $(Me_3Si)_2Si(H)Me$ and $(Me_3Si)_3SiH$. Values of $k_{(Me_3Si)_2Si(H)Me}/k_{(Me_3Si)_3SiH} = 0.46$ and $k_{(Me_3Si)_2Si(H)Me}/k_{Me_3SiSi(H)Me_2} = 4.3$ at 297 K were calculated from the loss of starting silanes by using the method of Ingold and Shaw.[26] Taking[27,28] $k_{Me_3SiSi(H)Me_2} = 1.7 \times 10^7$ and $k_{(Me_3Si)_3SiH} = 1.0 \times 10^8\ M^{-1}\ s^{-1}$ we obtained an average value of $k$ =

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(16) Errors correspond to 95% confidence limits (twice the standard deviation) but include only random and not systematic errors. It is worth pointing out that the high precision of the equation does not necessarily translate into similarly accurate kinetic values.

(17) The temperature-dependent function for cyclization of 5-hexenyl is:[18] $\log k_c(s^{-1}) = (10.42 \pm 0.32) - (6.85 \pm 0.42)/\Theta$, where $\Theta = 2.3RT$ kcal $mol^{-1}$.

(18) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

(19) Franz, J. A.; Barrows, R. D.; Camaioni, M. *J. Am. Chem. Soc.* **1984**, *106*, 3964.

(20) This rate constant was calculated from $k_r/k_{SnH} = 2.37 \times 10^{-3}$ M[19] and $k_{SnH} = 6.37 \times 10^6\ M^{-1}\ s^{-1}$. The latter rate constant was calculated from $Me_3CCH_2^\bullet + Bu_3SnH$ reaction given in ref 21.

(21) Johnson, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickeyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594.

(22) Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3578.

(23) Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399.

(24) Bond dissociation energies of $Bu_3Sn$–H,[25] $(Me_3Si)_3Si$–H,[11] and $Bu_3Ge$–H[13] are 308, 331, and 346 kJ $mol^{-1}$.

(25) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218.

(26) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918.

(27) Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Org. Chem.* **1986**, *51*, 2457.

(28) Chatgilialoglu, C.; Rossini, S. *Bull. Soc. Chim. Fr.* **1988**, 298.

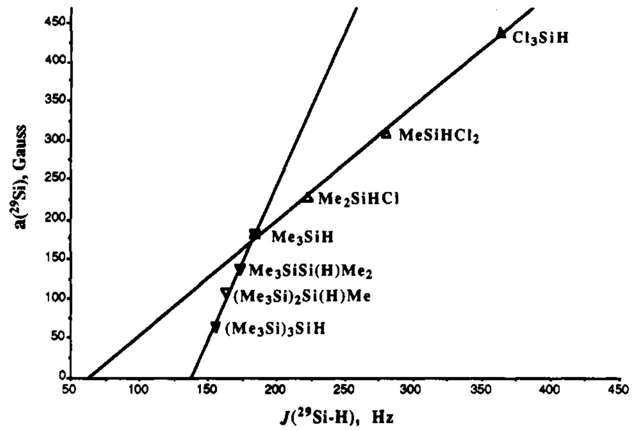

**Figure 3.** Correlation diagram between the $^{29}Si$ hyperfine splittings of silicon-centered radical and $J(^{29}Si-H)$ for the corresponding silanes.

$6 \times 10^7$ $M^{-1}$ $s^{-1}$ at 297 K for the reaction of *tert*-butoxyl radicals with $(Me_3Si)_2Si(H)Me$. Therefore, the rate constants for the reaction of *tert*-butoxyl radicals with $Et_3SiH$,[29] $Me_3SiSi(H)Me_2$,[27] $(Me_3Si)_2Si(H)Me$, and $(Me_3Si)_3SiH$[28] are (0.6, 1.7, 6, and 10) $\times 10^7$ $M^{-1}$ $s^{-1}$, respectively, at ambient temperature.[30] This trend indicates that the substitution of an alkyl group by a silyl group makes the reaction faster, this effect being cumulative.

**EPR Studies.** Photolysis of a solution of di-*tert*-butyl peroxide in $(Me_3Si)_2Si(H)Me$ (1:2 v/v) generates a paramagnetic species whose spectrum is shown in Figure 2. The spectral parameters, i.e., $g = 2.004\,51$, $a_H = 9.28$ G (3 H), $a_H = 0.44$ G (18 H), and $a(^{29}Si) = 90.3$ G (1 Si) allow us to identify this species as $(Me_3Si)_2\dot{S}iMe$ radical.[31] From the $^{29}Si$ hfs and literature[32] data we estimate that the unpaired electron resides in an orbital which has 5.5% of 3s-character.

Hudson et al.[33] have reported that a good correlation exists between the $^{29}Si$ hyperfine splitting of a silicon-centered radical and $J(^{29}Si-H)$ for the corresponding silanes.[34] The coupling constant $J(^{29}Si-H)$ is believed to be the sum of three terms;[37,38] that is, the interaction of orbital electronic currents with nuclear moments, the dipole–dipole interaction between nuclear and electron magnetic moments, and the Fermi contact interaction which is considered to be predominant. On the other hand, the hyperfine splitting $a(^{29}Si)$ is strictly related to the geometry of a silicon-centered radical.[39] Therefore, the correlation between $a(^{29}Si)$ and $J(^{29}Si-H)$ indicates the existence of a linear relation between the s-character of the single occupied molecular orbital (SOMO) and s-character of the silicon hybrid orbital of the parent silanes. Hudson et al.[33] also pointed out that inspection of the plot including all the available data shows that the values of $a(^{29}Si)$ for $(Me_3Si)_3Si^{\bullet}$ and $Cl_3Si^{\bullet}$ are significantly smaller than expected and suggested that electron delocalization onto the $Me_3Si$ or Cl in these radicals is responsible for this behavior.

We believe that correlations of this kind have a physical meaning only inside a family of compounds, i.e., $(Me_3Si)_{3-n}Si(H)Me_n$, $n = 0$–3. Thus, we plotted $a(^{29}Si)$ against $J(^{29}Si-H)$ for the two families of silanes where the Me groups in $Me_3SiH$ are successively substituted either with Cl or with $Me_3Si$. Figure 3 shows that there exists a very good correlation for the two classes of compounds; the lines are described by eqs 4 and 5 for the chloro- and trimethylsilyl-substituted compounds, respectively.

$$a(^{29}Si)/G = 1.453J(^{29}Si-H)/Hz - 91.5 \qquad r = 0.999 \tag{4}$$

$$a(^{29}Si)/G = 4.120J(^{29}Si-H)/Hz - 577.0 \qquad r = 0.998 \tag{5}$$

Rastelli and Pozzoli[40] have reported that in substituted silanes the s-character of the Si hybrid orbital is correlated with spin–spin coupling constants through the equation

$$J(^{29}Si-H) = 810a^2 \tag{6}$$

where $a^2$ is the s-character of the silicon hybrid orbital. Taking into consideration that the percentage of s-character (s%) in the SOMO of the radical is $a(^{29}Si)/-4594$ MHz,[32] combination of eqs 4 and 5 with 6 yields eqs 7 (Cl-substituted series) and 8 ($Me_3Si$-substituted series), respectively. Therefore, within each family the percentage

$$s\% = 0.720a^2 - 0.055 \tag{7}$$

$$s\% = 1.977a^2 - 0.377 \tag{8}$$

of s-character in the SOMO of the radicals is directly related to the s-character of the silicon hybrid orbital of the parent silanes. The fact that the percentage of s-character in the SOMO of silyl radicals is expected to change upon the degree of pyramidality of the radical center as well as upon delocalization of the unpaired electron into the remaining moieties does not allow us to obtain specific information on the electronic and geometrical properties of the radicals. However, while eqs 7 and 8 indicate that the overall effect is cumulative upon substitution within a family, their angular coefficients suggest that the change in geometry between the silyl radical and the parent silane is probably more marked on substituting Me with $Me_3Si$ than with Cl.

## Conclusions

$(Me_3Si)_2Si(H)Me$ is an effective reducing agent for organic halides, selenides, thionoesters, and isocyanides that functions by a free-radical chain mechanism. It is ca. 10 and 100 times less reactive than $(Me_3Si)_3SiH$ and $Bu_3SnH$, respectively, toward alkyl radicals and is expected to find place in organic synthesis when the desired product must be formed by a *slow* hydrogen transfer. Like its homologous, i.e., tris(trimethylsilyl)silane, it is expected to be more

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(30) These absolute values do not distinguish between sites or modes of interaction of silanes with *tert*-butoxyl radicals. It has been estimated that 92 and 95% of the attack occurs at the Si–H bond for $Me_3SiSi(H)Me$ and $(Me_3Si)_3SiH$, respectively.[28] Therefore, a similar behavior is expected from $(Me_3Si)_2Si(H)Me$.

(31) The EPR spectrum of $(Me_3Si)_2\dot{S}iMe$ radical has been previously reported (Cooper, J.; Hudson, A.; Jackson, R. A. *Mol. Phys.* **1972**, *23*, 209). Although the reported $g = 2.0045$ and $a_H = 9.36$ G (3 H) are in agreement with our spectrum, the $a(^{29}Si) = 71$ G does not fit the spectrum shown in Figure 2.

(32) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(33) (a) Hudson, A.; Jackson, R. A.; Rhodes, C. J.; Del Vecchio, A. L. *J. Organomet. Chem.* **1985**, *280*, 173. (b) See also: Johnson, K. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1111.

(34) Similar correlations have proved successful for investigating the structures of carbon-[35] and phosphorus-centered[36] radicals.

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(40) Rastelli, A.; Pozzoli, S. A. *J. Mol. Struct.* **1973**, *18*, 469.

acceptable than triorganotin compounds from toxicological and practical perspectives. Further work on the synthetic scope of this material is in progress.

## Experimental Section

**Materials.** 1,1,1,2,3,3,3-Heptamethyltrisilane,[41] cyclohexyl selenide,[42] cyclohexyl xanthate,[43] neophyl bromide,[44] and di-*tert*-butyl hyponitrite[45] were prepared following literature procedures. $(Me_3Si)_2Si(D)Me$ was obtained from the corresponding silyl chloride[41] and $LiAlD_4$. All other materials were commercially available and used as received.

**General Procedure for Reduction of Organic Derivatives (Table I).** A solution containing the compound to be reduced, $(Me_3Si)_2Si(H)Me$ (1.2 equiv), and AIBN (10–20%) as initiator in toluene or benzene was heated at 348–363 K for 0.5–2.5 h and then analyzed by GC. Yields were quantified by GC using dodecane or tetradecane as an internal standard.

**General Procedure for Kinetic Measurement.** *tert*-Butylbenzene containing a small amount of decane as an internal GC standard was used as solvent. In the case of neophyl bromide, benzene was used as solvent. $(Me_3Si)_2Si(H)Me$ was added at concentrations between 1.2 and 4 M, and the bromides were added in a ratio of ca. 1:20 respect to the silane. Samples of the reaction mixtures were degassed and sealed under nitrogen in Pyrex ampules and were thermolyzed or photolyzed. Reaction were initiated thermally at 313, 323, 333 (di-*tert*-butyl hyponitrite), 350, 373 (AIBN), and 393 K (*tert*-butyl perbenzoate) and photolytically at 298 K. The products of the reaction were analyzed by GC chromatography using a 15-m × 0.53-mm methyl phenyl 5% column (Quadrex) with temperature programming from 40 to 250 using a Varian 3300 chromatograph. The hydrocarbon products of interest were identified by comparison of their retention times with authentic material.

**EPR Measurements.** The $(Me_3Si)_2\dot{S}iMe$ radical was generated by photolysis of solution of di-*tert*-butyl peroxide and $(Me_3Si)_2Si(H)Me$ (1:2 v/v) at 233 K in the cavity of a Bruker ESP300 spectrometer equipped with an NMR gaussmeter, a frequency counter, and a standard variable-temperature device. A 500-W high-pressure mercury lamp was used as UV light source. The spectrum was recorded using 200 G scan width and the regions to the left and to the right of the main pattern were recorded at higher gain. The other $^{29}Si$ hfs shown in Figure 3 were taken from ref 46.

**IR and NMR Measurements.** IR and NMR spectra of $(Me_3Si)_2Si(H)Me$ were recorded on Nicolet FTIR and Varian VXR200 spectrometers. The SiH stretching frequency and coupling constant are 2075 cm$^{-1}$ and 163 Hz, respectively. The analogous data for $Me_3SiSi(H)Me_2$ and $(Me_3Si)_3SiH$ were taken from refs 47 and 48, respectively. The SiH stretching frequencies for the series $Me_{3-n}SiH_{n+1}$ were taken from ref 9, and the SiH coupling constants for the series $Me_{3-n}Si(H)Cl_n$ were taken from ref 37.

**Acknowledgment.** Financial support from the Progetto Finalizzato Chimica Fine II (CNR–Rome) is gratefully acknowledged.

**Supplementary Material Available:** Tables IV–VI giving detailed product ratios of kinetics (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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# Highly Regioselective and Stereospecific Functionalization of 1,2-Propanediol with Trimethyl(X)silanes Employing the 1,3,2λ$^5$-Dioxaphospholane Methodology

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*Received January 10, 1992*

The regioselective ring opening of (*S*)-4-methyl-2,2,2-triphenyl-1,3,2λ$^5$-dioxaphospholane (**2**) [prepared from the bis(transoxyphosphoranylation) of (*S*)-1,2-propanediol (**1**) with diethoxytriphenylphosphorane (DTPP)] was initiated with several trimethylsilyl reagents ($Me_3SiX$: X = PhS, I, Br, Cl, CN, and $N_3$) to afford the regioisomeric (silyloxy)phosphonium salts. A stereospecific extrusion of triphenylphosphine oxide from these oxyphosphonium salts gave predominantly the thermodynamically less stable C-2-X-substituted derivatives with nearly complete inversion of stereochemistry at the C-2 stereogenic center (i.e., X = PhS).

## Introduction

A highly regio- and stereospecific method for C-2 hydroxyl replacement in an unsymmetrical 1,2-diol [i.e., 1,2-propanediol (**1**)] in a "single synthetic event" would be of significance for effecting a host of useful synthetic transformations. Previously, we described the benzoylation of diol **1** and 2-phenyl-1,2-ethanediol with triphenylphosphine and benzoyl peroxide. The intermediate and transient 4-methyl- (**2**) and 4-phenyl-2,2,2-triphenyl-1,3,2λ$^5$-dioxaphospholanes, respectively,[1] were captured with the benzoic acid, formed in situ, to afford largely the C-2 benzoate with essentially complete inversion of stereochemistry.[1] We suggested that an association (i.e., intermolecular hydrogen bonding) between the dioxaphos-

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0022-3263/92/1957-3409$03.00/0 © 1992 American Chemical Society