

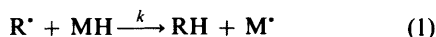
Organosilanes as Radical-based Reducing Agents with Low Hydrogen Donating Abilities

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$\text{Me}_3\text{SiSi}(\text{H})\text{Me}_2$, $\text{Me}_3\text{SiSiMe}_2\text{Si}(\text{H})\text{Me}_2$, and $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{H})\text{Me}_2$ have been used as radical-based reducing agents for a variety of organic substrates. Rate constants for the reaction of primary alkyl radicals with these silanes have been measured over a range of temperature by using the neophyl rearrangement as a radical clock. Some kinetic data have also been obtained for phenyl substituted silanes. The experimental findings are complemented by *ab initio* MO studies, at different levels of theory, which predict the Si–H bond dissociation energies of PhSiH_3 , Ph_2SiH_2 , and $\text{XSiH}_2\text{SiH}_2\text{H}$, where X = H, Me and SiH_3 . The radical trapping abilities of these silanes and other common radical-based reducing agents are compared.

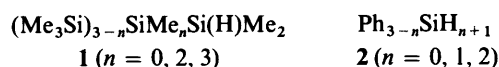
Free radical reactions have gained distinction in new synthetic methodology and have been the focus of many recent important studies.¹ In order to evaluate whether specific free-radical chain reactions are synthetically useful, kinetic or thermodynamic knowledge of each propagation step must be considered.¹ The key step for the majority of radical reactions under reducing conditions is reaction (1), Bu_3SnH being the most frequently



used reducing agent.¹ However, there are several problems associated with triorganotin reagents, the main ones being tin residues and toxic waste.² Occasionally other organometallic hydrides such as Bu_3GeH ³ and RHgH ⁴ have been applied as complements to Bu_3SnH . In the last few years, tris(trimethylsilyl)silane, TTMSS, has proved to be a valid alternative to tin hydrides for the majority of its radical chain reactions although in a few cases the two reagents can complement each other.² Following the success of TTMSS,² it was thought that other organosilanes having a wide range of hydrogen donor abilities, might be capable of sustaining analogous radical chain reactions. In fact, we have recently shown that $(\text{Me}_3\text{Si})_3\text{SiSH}$ ⁵ and $(\text{Me}_3\text{Si})_2\text{Si}(\text{H})\text{Me}$ ⁶ can be used as reducing agents having, respectively, high and low hydrogen donor abilities. Barton *et al.*⁷ have shown that phenyl substituted silanes can be used as reducing agents for the deoxygenation of alcohols *via* the corresponding thionocarbonates or xanthates. Therefore, use of organosilanes that promote free radical chain reactions is an emerging methodology for organic transformations.²

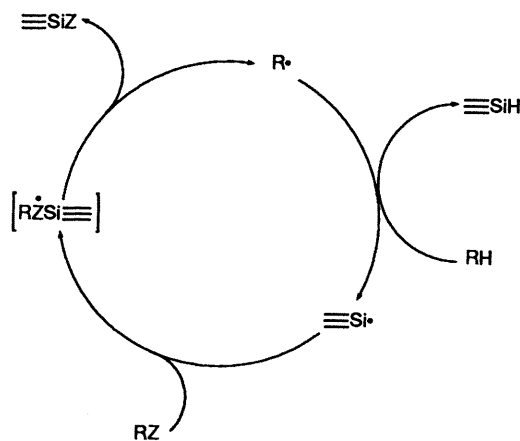
When designing new radical reactions one is faced with the difficult task of selecting the reducing agent and particular experimental conditions depending upon the hydrogen donation ability of the hydrides. Two examples: (i) the stereoselectivities of radical reactions can be steered by varying the hydrogen donors as well as the reaction temperature and the β -substituent;⁸ (ii) rapid hydrogen transfer is not an advantage when the synthetic strategy requires another radical reaction to take place before the hydrogen transfer step. Therefore, slowness may be a desirable characteristic given the limitation that the reaction must proceed with reasonable chain length to give decent yields. In the present work, we have investigated in some detail the two series of silanes 1 and 2 as radical reducing agents having low hydrogen donating abilities. For the former series, a kinetic study on the formation and further reaction of pentamethylsilyl radical, *i.e.* 1 where $n = 3$, has been reported by Ingold and co-workers.⁹ For the latter series, Barton *et al.*⁷

employed PhSiH_3 and Ph_2SiH_2 for the deoxygenation of alcohols, whereas Griller and co-workers,¹⁰ based on a kinetic study, indicate that PhMe_2SiH and Ph_2MeSiH are impractical reducing agents. Therefore, our aims are to find out which of these compounds are practical agents under *normal* conditions, and to obtain some information on the effect of successive β -trimethylsilyl substitution on pentamethyldisilane and of successive phenyl substitution at the Si–H function.



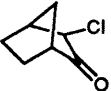

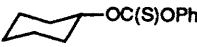

Results

Reduction of Organic Derivatives with Silanes 1.—Reduction of a variety of organic derivatives were carried out by using silanes 1, where $n = 0, 2, 3$. Reactions of each derivative with the appropriate silane at 95–125 °C in toluene or *tert*-butylbenzene and in the presence of a radical initiator, *i.e.* dibenzoyl peroxide or *tert*-butyl perbenzoate, gave the corresponding hydrocarbons in good yields (see Table 1). AIBN was found not to be a good radical initiator for these reactions. Sample analyses were carried out using GC with authentic samples as calibrants. Yields and conversions were quantified by using an internal standard. Evidence for a free radical chain mechanism (Scheme 1) was provided by the observation that the reactions were catalysed by thermal sources of free radicals



Scheme 1

Table 1 Reduction of some organic derivatives by silanes 1

Substrate	Me ₃ SiSi(H)Me ₂		Me ₃ SiSiMe ₂ Si(H)Me ₂		(Me ₃ Si) ₃ SiSi(H)Me ₂	
	Method ^a	Yield ^b (%)	Method ^a	Yield ^b (%)	Method ^a	Yield ^b (%)
	A	83	B	87 ^c	C	83
C ₁₆ H ₃₃ Br	A	90	A	82	C	93
C ₁₆ H ₃₃ I	A	88	A	80	A	90
	A	71	A	82	A	70
	B	90	B	95	B	100
	A	85 ^d	A	96 ^d	A	82 ^d

^a Method A: Initiator = PhC(O)OOCMe₃ (15%), *T* = 125 °C, solvent = PhCMe₃. Method B: Initiator = (PhCO₂)₂ (15%), *T* = 95 °C, solvent = PhCH₃. Method C: Initiator = PhC(O)OOCMe₃ (15%), *T* = 100 °C, solvent = PhCH₃. ^b Yields are based on the formation of corresponding hydrocarbon and on the amount of substrate converted. Conversions and yields were quantified by GC using decane or tetradecane as an internal standard. Conversions, which are based on disappearance of the starting material, are quantitative unless otherwise stated. ^c Conversion 75%. ^d Conversion 45–55%.

Table 2 Arrhenius expressions for the reaction of neophyl radical with some silanes

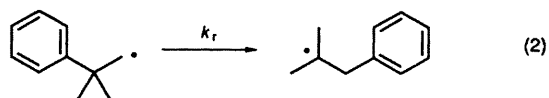
Silane	<i>T</i> range, K	Relative rate expression, log[(<i>k_r</i> / <i>k_H</i>)/mol dm ⁻³] ^{a,b}	Absolute rate expression, log(<i>k_H</i> /dm ³ mol ⁻¹ s ⁻¹) ^{a,b,c}
Me ₂ SiSi(H)Me ₂	348–428	(2.52 ± 0.36) – (4.34 ± 0.66)/θ	(9.03 ± 0.68) – (7.48 ± 1.14)/θ
Me ₃ SiSiMe ₂ Si(H)Me ₂	348–418	(2.56 ± 0.48) – (4.66 ± 0.84)/θ	(8.99 ± 0.80) – (7.16 ± 1.32)/θ
(Me ₃ Si) ₃ SiSi(H)Me ₂	348–423	(2.95 ± 0.34) – (5.19 ± 0.58)/θ	(8.60 ± 0.66) – (6.63 ± 1.06)/θ

^a θ = 2.3 *RT* kcal mol⁻¹. ^b 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. ^c These absolute values do not distinguish between sites or modes of interaction of silanes with neophyl radicals. [It has been estimated in ref. 9 that > 90% of the attack occurs at the SiD bond for Me₃SiSi(D)Me₂ at 120 °C.]

such as *tert*-butyl perbenzoate 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. Structure [RZSi≡] may represent a reactive intermediate or a transition state (*cf.* ref. 11).

Reaction of Primary Alkyl Radicals with Silanes 1 and 2.—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).¹² 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.

The neophyl bromide was chosen as precursor of primary alkyl radicals since its unimolecular reaction [eqn. (2)] has been



studied in detail (*vide infra*). The neophyl radical was formed from the corresponding bromide and the appropriate silane by a thermally initiated or photoinitiated radical chain reaction in 1,3-di-*tert*-butylbenzene as the solvent. The two hydrocarbon

products were *tert*-butylbenzene and isobutylbenzene, the relative concentrations of which varied in the expected manner at each temperature as the concentration of silane was changed. If the silane is the only source of hydrogen atoms and if its concentration does not change significantly during an experiment, then eqn. (3) holds. Since our experimental

$$[\text{silane}] = \frac{k_r}{k_H} \frac{[\text{PhCMe}_3]}{[\text{PhCH}_2\text{CHMe}_2]} \quad (3)$$

conditions meet these requirements, mean values of the *k_r*/*k_H* ratio were obtained at different silane concentrations according to eqn. (3). Silanes 1 and 2 were used for these measurements. The detailed results of the individual experiments as well as the further kinetic treatment are available as supplementary material.* Analysis of these data yields the relative kinetic parameters which are reported in column 3 of Table 2 and column 2 of Table 3 for β-trimethylsilyl substituted disilanes and α-phenyl substituted silanes respectively. The absolute values of the rate constants for H atom abstraction from silanes 1 and 2 by the neophyl radical, *i.e.* *k_H*, can be obtained by combining these data with the rate constants for the neophyl rearrangement. The Arrhenius parameters for the latter rearrangements have been obtained by Franz *et al.*¹³ as a result of a careful study of the Bu₃SnH/neophyl chloride reaction [eqn. (4)], and are based on the assumption that the neophyl

* Supp. Pub. No. 56920, 16 pp. For details of the Supplementary Publication Scheme see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

Table 3 Kinetic parameters for the reaction of neophyl radical with some silanes at 383 K

Silane	$(k_t/k_H)/\text{mol dm}^{-3} \text{ s}^{-1}$	$k_H/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
PhSiH ₃	2.196 ± 0.141	2.9 × 10 ⁴
Ph ₂ SiH ₂	1.147 ± 0.106	5.6 × 10 ⁴
Ph ₃ SiH	1.438 ± 0.100	4.6 × 10 ⁴

^a Errors correspond to one standard deviation.

$$\log(k_t/s^{-1}) = (11.55 \pm 0.32) - (11.82 \pm 0.48)/\theta \quad (4)$$

radical will react with Bu₃SnH at the same rate as that measured for primary alkyl radicals.¹⁴ Absolute kinetic parameters from the reaction of neophyl radical with silanes 1 and 2 are also given in Tables 2 and 3.

EPR Studies.—Photolysis of a solution of di-*tert*-butyl peroxide in Me₃SiSiMe₂Si(H)Me₂ (1:2 v/v) generates a paramagnetic species whose spectrum shows the following parameters at 233 K: $a_H = 8.0$ G (6 H), $a(^{29}\text{Si}) = 134.2$ G, $g = 2.00379$. Based on the similarity of these parameters with the ones of the previously reported spectrum of Me₃SiSiMe₂,¹⁵ *i.e.* $a_H = 8.2$ G (6 H), $a_H = 0.47$ G (9 H), $a(^{29}\text{Si}) = 137$ G, $g = 2.0037$, we identify this species as Me₃SiSiMe₂SiMe₂ radical. On the other hand, photolysis of a solution of (Me₃Si)₃SiSi(H)Me₂ and di-*tert*-butyl peroxide yields a very complicated spectrum due to superimposition of more than one radical.

Theoretical Evaluation of Bond Dissociation Energies (BDE).—The Si–H bond strength in silanes was experimentally found to be sizably reduced by successive α -silyl substitution.^{16,17} Based on physical chemical knowledge, the origin of this phenomenon was interpreted in terms of through-bond and through-space interactions.¹⁸ Afterwards, based on a theoretical study, a through-space (conjugation) interaction between low-lying empty orbitals or high-lying lone pairs and the radical centre was found to decrease greatly the BDE(Si–H).¹⁹ It is therefore conceivable that the BDE(Si–H) could be reduced by substituents X, located in the β -position owing to a through-space (hyperconjugation) interaction between the bonding and/or antibonding Si–X MOs and the radical centre.

As the hyperconjugative effect of β -substituents on the BDE(Si–H) could be related to the electron transfer between the radical centre and the $\sigma^*_{\text{Si-X}}$ orbital, we then carried out MO calculations on XSiH₂SiH₂[•], where X = H, CH₃, SiH₃, model compounds using the GAUSSIAN 86 series of programs.²⁰ Geometries optimized at different levels of theory for both the silanes and the corresponding silyl radicals are reported in supplementary material. Inspection of geometries shows that β -substituents do not affect significantly the structural parameters of the radical centre, which is pyramidal. The angle φ (see Fig. 1) which defines the degree of pyramidity is slightly larger than the tetrahedral value; that is, φ is equal to 134.0, 134.6, and 132.6° for X = H, CH₃, SiH₃, respectively, at the highest level of theory (6-31G*), as compared with 125.3° for the tetrahedral configuration. The β -substituent eclipses the SOMO in an anti position so as to minimize the bonding electron pair repulsion (*gauche* effect) as previously found in third-row β -substituted alkyl radicals.²¹

The gross Mulliken population in the SOMO shows that a significant charge transfer from the radical centre to the XSiH₂ moiety occurs (Table 4). In particular, the effect of the substitution of a hydrogen by a methyl group on the electron transfer is small and it significantly increases with the β -silyl substitution. This result suggests that β -silyl substituents can sizably reduce the BDE(Si–H). However, the ²⁹Si coupling

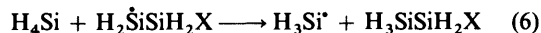
Table 4 Electron charge distribution in the SOMO of XSiH₂SiH₂[•] radicals at the 6-31G* level

	–SiH ₂ [•]	–SiH ₂ –	X
H	0.881 62	0.080 81	0.037 57
CH ₃	0.870 11	0.082 01	0.047 88
SiH ₃	0.785 28	0.107 08	0.107 64

**Fig. 1**

constants computed with *ab initio* 6-31G* basic set are consistent with a small effect of the β -substituent in anti position with respect to the SOMO, the ²⁹Si hfs being computed to be 152.3, 148.9, and 157.9 G for X = H, CH₃, and SiH₃. These values decrease with increasing electronegativity of the substituents.

The influence of the substituents X on the BDE(XSiH₂SiH₂–H) has been estimated by means of the isogyric reaction (6).



The calculations in Table 5 show the results at different levels of theory. In both HF/STO-3G* and HF/6-31G* levels the introduction of a β -methyl substituent does not affect significantly the BDE(Si–H) whereas the β -silyl substituent decreases it slightly. Electron correlation, both at second and fourth order perturbation theory, has a small effect on BDEs. It is worth pointing out that since eqn. (6) is isodesmic, cancellation of errors owing to electron correlation makes the relative BDEs more accurate than any computed BDEs in absolute scale.

Using the same approach, the influence of the α -phenyl substituent on the BDE(Si–H) was estimated next. Optimized geometries for PhSiH₃ and Ph₂SiH₂ as well as for the corresponding silyl radicals are reported in supplementary material. In particular, we have computed the BDE(Si–H) of PhSiH₃ and Ph₂SiH₂ only at the HF/STO-3G* and MP2/STO-3G* levels as the systems are relatively large (see Table 5). The computed 1.55 kcal mol^{–1} reduction of the BDE(Si–H) going from SiH₄ to PhSiH₃ is unaffected by further phenyl substitution.†

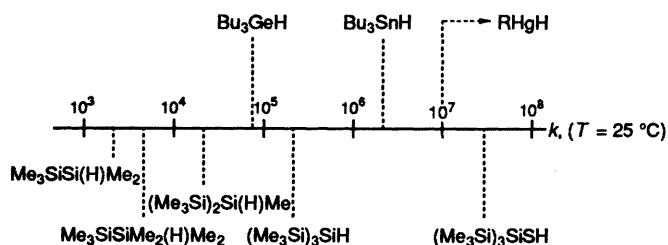
Discussion

The Arrhenius expressions for the reaction of neophyl radical with silanes 1 are reported in Table 2. For Me₃SiSi(H)Me₂ we calculate a rate constant of 7.4 × 10⁴ dm³ mol^{–1} s^{–1} at 120 °C which is in satisfactory agreement with the value of 1.0 × 10⁵ dm³ mol^{–1} s^{–1} reported by Ingold⁹ at this temperature. The Arrhenius preexponential factors all lie in the expected range and show the anticipated decrease with increasing steric hindrance in the starting materials. The decrease of activation enthalpies with successive β -Me₃Si substitution is probably due to the decrease of BDEs. At 25 °C, we calculate rate constants of 3.5, 5.5 and 5.5 × 10³ dm³ mol^{–1} s^{–1} for Me₃SiSi(H)Me₂, Me₃SiSiMe₂Si(H)Me₂, and (Me₃Si)₃SiSi(H)Me₂, respectively, indicating that although the mono- β -Me₃Si substitution increases slightly the hydrogen donation ability, the multi- β -

† 1 cal = 4.184 J.

Table 5 Bond dissociation energies of some silanes relative to SiH₄ at different levels of theory

Level	Δ BDE for eqn. (6)/kcal mol ⁻¹			Δ BDE/kcal mol ⁻¹	
	H ₃ SiSiH ₃	CH ₃ SiH ₂ SiH ₃	H ₃ SiSiH ₂ SiH ₃	PhSiH ₃	Ph ₂ SiH ₂
HF/STO-3G*/STO-3G*	-2.81	-2.85	-3.24	-1.38	-1.41
MP2/STO-3G*/STO-3G*	-3.12	-3.24	-3.69	-1.55	-1.55
MP4/STO-3G*/STO-3G*	-3.21	-3.34	-3.79		
HF/6-31G**/6-31G*	-2.90	-2.98	-3.19		
MP2/6-31G**/6-31G*	-2.94	-3.01	-3.23		
MP4/6-31G**/6-31G*	-2.96	-3.03	-3.26		

**Fig. 2** Rate constants for hydrogen abstraction from a variety of reducing agents by primary alkyl radicals at 25 °C. For RHgH, the value is larger than $1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Me₃Si substitution has no effect on the rate constant in the temperature range of interest.

The Δ BDEs in Table 5 are actually the energies for reaction (6) computed at different levels of theory. The introduction of a β -methyl substituent does not affect significantly the BDE(Si-H) whereas the introduction of a β -silyl substituent decreases it slightly. The fact that β -substitution has a small effect on BDEs indicates that either the hyperconjugative interaction modifies to the same extent the intrinsic stability of the radical and of the molecule with its intact bond, or that β -hyperconjugative interactions have a small effect on BDEs. It is noteworthy that the trend of the theoretical BDEs (at all levels of theory) agrees very well with the kinetic findings.

The reduction of a variety of organic substrates such as chlorides, bromides, iodides, isocyanides, thionoesters, and selenides can be performed in good yields by using silanes **1** as reducing agents (see Table 1). However, the reaction condition requires excess of the appropriate silane and preferably *tert*-butyl perbenzoate as initiator at 125 °C, in agreement with short chain lengths due to the low hydrogen donation abilities of these silanes.

The rate constants for the reaction of neophyl radical with phenyl substituted silanes are reported in Table 3. Although the values are very close to each other, the trend of reactivity Ph₂SiH₂ > Ph₃SiH > PhSiH₃ is the same as that obtained for the reaction of *tert*-butoxyl radical with these silanes.²² Furthermore, taking into account the statistical number of hydrogens abstracted we calculated 1.0, 2.8 and $4.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for PhSiH₃, Ph₂SiH₂ and Ph₃SiH, respectively (relative rates per H atom). These values are in satisfactory agreement with rate constants (at 90 °C) of 1.1, 1.9 and $3.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reactions of the primary alkyl radical with PhSi(H)Me₂, Ph₂Si(H)Me, and Ph₃SiH respectively, which were obtained recently by Griller *et al.* by applying a different approach.¹⁰ Table 5 shows that the Si-H bond strength in PhSiH₃ is *ca.* 1.5 kcal mol⁻¹ lower than in H₄Si, the result being in agreement with the experimental values of 1.4 and 2 kcal mol⁻¹.¹⁷ We also found similar results for Ph₂SiH₂, indicating that the presence of the second phenyl group has no effect. Although theoretical and kinetic data are in reasonable agreement, it was recently mentioned¹⁰ that the Si-H bond in Ph₃SiH is *ca.* 84 kcal mol⁻¹, and therefore is *ca.* 7 kcal mol⁻¹

lower than that in H₄Si, which is somewhat in contradiction with the present kinetic data.²³ The origin of this discrepancy is unknown.* Based on the present kinetic data, the reaction chain lengths for the reduction of organic substrates by phenyl substituted silanes, under normal conditions, would be unacceptably small. The fact that large quantities of initiator (1–2 equiv.) are needed for the deoxygenation of secondary alcohols *via* thionoesters using Ph₂SiH₂ or PhSiH₃ as reducing agents⁷ confirms that these reactions have very short chain lengths. A further handicap for the use of these silanes as reducing agents is that all of the phenyl substituted silyl radicals add readily to the aromatic rings of their precursors and to the aromatic rings of the solvent (benzene or toluene are most commonly used in synthesis *via* radicals) with rate constants *ca.* $10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.²² Consequently, only substrates that react with silyl radicals in the proximity of diffusion control can be employed.

Fig. 2 reports rate constants for hydrogen abstraction from a variety of reducing agents by primary alkyl radicals [*cf.* eqn. (1)] at ambient temperature. In the upper part of the diagram the reactivities of germanium, tin and mercury hydrides are shown. Primary alkyl radicals abstract H atom from Bu₃GeH,²⁴ Bu₃SnH,¹⁴ and RHgH²⁵ with rate constants (at 25 °C) of 9.3×10^4 , 2.3×10^6 and $> 1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. In the lower part of the diagram the reactivities of a variety of organosilanes are reported. The rate constants of primary alkyl radicals with these silanes cover a range of four orders of magnitude.† In our opinion, if a synthetic strategy requires a slow hydrogen donor, Me₃SiSi(H)Me₂ and Ph₂SiH₂ are at the limits of practical value. In conclusion, the Si-H bond strength in organosilanes can be modulated by the substituents, and therefore a wide range of hydrogen donor abilities is possible.

Experimental

Materials.—Me₃SiSi(H)Me₂,²⁷ Me₃SiSiMe₂Si(H)Me₂,²⁷ (Me₃Si)₃SiSi(H)Me₂,²⁸ cyclohexyl selenide,²⁹ cyclohexyl xanthate,³⁰ neophyl bromide³¹ and di-*tert*-butyl hyponitrite³² were prepared following literature procedures. All other materials were commercially available and used as received.

General Procedure for Reduction of Organic Derivatives (Table 1).—A solution containing the compound to be reduced (0.1–0.3 mol dm⁻³), the appropriate silane (4 equiv.) and radical initiator (15%) in toluene or *tert*-butylbenzene was heated for 2 h and then analysed by GC. The products of interest were identified by comparison of their retention times with authentic material. Yields were quantified by GC using dodecane or tetradecane as an internal standard.

General Procedure for Kinetic Measurement.—1,3-Di-*tert*-

* To our knowledge the original source of BDE(Ph₃Si-H) *ca.* 84 kcal mol⁻¹ is still unpublished (*cf.* ref. 6 of the Griller's paper).¹⁰

† For (Me₃Si)₃SiSH see ref. 5. For (Me₃Si)₃SiH see ref. 26. For (Me₃Si)₂Si(H)Me see ref. 6.

butylbenzene containing a small amount of nonane as an internal GC standard was used as solvent. The appropriate silane and the neophyl bromide were added in a ratio of ca. 20:1. *tert*-Butyl hyponitrite, dibenzoyl peroxide, *tert*-butyl perbenzoate and *tert*-butyl peroxide were used as radical initiators depending on the reaction temperature. Samples of the reaction mixtures were degassed and sealed under nitrogen in Pyrex ampoules and were thermolysed. The products of the reaction were analysed by GC chromatography using a 15 m × 0.53 mm methyl phenyl 5% column (Quadrex) with temperature programming from 40 to 250 °C using a Varian 3300 chromatograph. The hydrocarbon products of interest were identified by comparison of their retention times with authentic material.

EPR Measurements.—The $\text{Me}_3\text{SiSiMe}_2\dot{\text{S}}\text{SiMe}_2$ radical was generated by photolysis of solution of di-*tert*-butyl peroxide and $\text{Me}_3\text{SiSiMe}_2\text{Si}(\text{H})\text{Me}_2$ (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 a 200 G scan width and the regions to the left and to the right of the main pattern were recorded at higher gain.

Acknowledgements

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