J. Org. Chem. 1993, 58, 249–251

# A Comment on the Use of Triethylsilane as a Radical-Based Reducing Agent

Chryssostomos Chatgilialoglu,*[1] Carla Ferreri,[2] and Marco Lucarini[1,3]

*I.Co.C.E.A., Consiglio Nazionale delle Ricerche, Via della Chimica 8, 40064 Ozzano Emilia (Bologna), Italy, and Dipartimento di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, 80134 Napoli, Italy*

*Received July 20, 1992*

## Introduction

Organosilanes that promote free-radical chain reactions are an emerging methodology for organic transformations.[4] For example, $(Me_3Si)_3SiH$ has been used in recent years as an alternative or complementary to $Bu_3SnH$ in free-radical reactions. The key step for the majority of these transformations is

$$R^{\bullet} + {\equiv}SiH \rightarrow RH + {\equiv}Si^{\bullet} \qquad (1)$$

Based on thermodynamic,[5] kinetic,[6,7] and product studies,[8] it was suggested that trialkylsilanes are poor reducing agents in free-radical chain processes.[4] That is, although trialkylsilyl radicals are among the most reactive species toward various organic functional groups,[9] the corresponding silanes are rather poor H atom donors toward alkyl radicals[6,7] and therefore do not support chain reactions under *normal* conditions. Recently, Barton et al.[10] found that $Et_3SiH$ can be used as reducing agent, in particular for the deoxygenations of alcohols via thiocarbonates and xanthates, and a mechanistic scheme was proposed where reaction 1 represents the key step. In order to throw some light on this discrepancy, we reinvestigated the procedure of Barton et al.[10] from a mechanistic point of view.

## Results and Discussion

**A Kinetic Study of the Reaction of $Et_3SiH$ with a Primary Alkyl Radical.** To measure the Arrhenius parameters of the reaction of $Et_3SiH$ with a primary alkyl radical we chose the neophyl rearrangement (eq 2) as our free-radical clock,[11] since it has been studied in detail by Franz et al.[12] and it has been employed with success for similar purposes by Ingold and co-workers.[6] The neophyl

$$PhCMe_2CH_2^{\bullet} \xrightarrow{k_r} {}^{\bullet}CMe_2CH_2Ph \qquad (2)$$

radical was formed from the corresponding bromide and the silane by a thermally initiated radical chain reaction in 1,3-di-*tert*-butylbenzene as the solvent.[15] By measuring the relative yields of *tert*-butylbenzene and isobutylbenzene at various $Et_3SiH$ concentrations, under conditions in which silane is the only source of hydrogen and its concentration does not change significantly during an experiment, we obtained the following Arrhenius expression in the temperature range of 323–418 K:

$$\log (k_r/k)(\mathrm{M}) = (2.89 \pm 0.26) - (3.84 \pm 0.44)/\Theta \qquad (3)$$

where $\Theta = 2.3RT$ kcal mol$^{-1}$ and the errors correspond to 95% confidence limits.[17] The detailed results of the individual experiments and the subsequent kinetic treatment are available as supplementary material. The absolute value of the rate constants for H atom abstraction from $Et_3SiH$ by the primary alkyl radical, i.e., $k$, can be obtained by combining eq 3 with the Arrhenius equation for the neophyl rearrangement.[12] These results are reported in Table I together with the analogous data for *tert*-butoxyl and trichloromethyl radicals for comparison.

The Arrhenius preexponential factors are all the same and lie in the expected range.[20] The neophyl radical is slightly more reactive than $Cl_3C^{\bullet}$ and 4 orders of magnitude less reactive than $Me_3CO^{\bullet}$, presumably because the bond strength in $Me_3CO{-}H$ is ca. 7 and 9 kcal mol$^{-1}$ larger than that of $RCH_2{-}H$ and $Cl_3C{-}H$, respectively.[21] The difference in bond strength manifests itself in enthalpies of activation; i.e., the larger activation energies for the neophyl and trichloromethyl radicals must be due to the fact that such reactions are less exothermic.[22] Previously, an approximate value of $7 \times 10^3$ M$^{-1}$ s$^{-1}$ at 323 K for the reaction of cyclopentylmethyl radical with $Et_3SiH$ was obtained,[7] which is in reasonable agreement with the value

---

[1] Consiglio Nazionale delle Ricerche.

[2] Università di Napoli.

[3] Present address: Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, Via S. Donato 15, 40127 Bologna, Italy.

[4] Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188.

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

[6] Lusztyk, J.; Maillard, B.; Ingold, U. K. *J. Org. Chem.* **1986**, *51*, 2457.

[7] Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132.

[8] Chatgilialoglu, C. Unpublished results.

[9] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5119 and 5123; *J. Am. Chem. Soc.* **1983**, *105*, 3292; *J. Org. Chem.* **1987**, *52*, 938.

[10] (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1991**, *32*, 7187. (b) See also: Barton, D. H. R. *Tetrahedron* **1992**, *48*, 2529 and references cited therein.

[11] 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.

[12] The Arrhenius parameters for the neophyl rearrangement have been obtained by Franz et al.[13] as a result of careful study of the $Bu_3SnH$/neophyl chloride reaction: $\log (k_r/\mathrm{s}^{-1}) = (11.55 \pm 0.32) - (11.82 \pm 0.48)/\Theta$, and are based on the assumption that the neophyl radical will react with $Bu_3SnH$ at the same rate as that measured from primary alkyl radicals.[14]

[13] Franz, J. A.; Barrows, R. D.; Camaioni, M. *J. Am. Chem. Soc.* **1984**, *106*, 3964.

[14] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

[15] 1,3-Di-*tert*-butylbenzene was chosen as a solvent because of its relatively high boiling point and its slow thermoneutral reaction with neophyl radical. The hydrogen abstraction from $CH_3$, $CH_2$, and SiH moieties of $(CH_3CH_2)_3SiH$ by the neophyl radical are exothermic by ca. 5, 6, and 10 kcal mol$^{-1}$. In fact, $\alpha$- and $\beta$-stabilization effect of silicon on the alkyl radicals are ca. 0.4 and 2.9 kcal mol$^{-1}$.[16]

[16] Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

[17] 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.

[18] Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* **1982**, *1*, 466.

[19] Baruch, G.; Horowitz, A. *J. Phys. Chem.* **1980**, *84*, 2535.

[20] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

[21] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[22] The hydrogen atom abstraction from the SiH moiety of $Et_3SiH$ by primary alkyl, *tert*-butoxyl, and trichloromethyl radicals are exothermic by 8, 15, and 6 kcal mol$^{-1}$, respectively; these estimates being based on bond dissociation energies for $Et_3Si{-}H$,[5] $RCH_2{-}H$,[21] $Me_3CO{-}H$,[21] and $Cl_3C{-}H$[21] of 90, 98, 105, and 96 kcal mol$^{-1}$, respectively.

0022-3263/93/1958-0249$04.00/0

**Table I. Kinetic Parameters for the Reaction of Some Radicals with $Et_3SiH$**

| radical | log *A*, $M^{-1}$ $s^{-1}$ | $E_a$, kcal $mol^{-1}$ | $k^{298}$, $M^{-1}$ $s^{-1}$ | ref |
|---|---|---|---|---|
| $PhCMe_2CH_2^\bullet$ | $8.66 \pm 0.58$ | $7.98 \pm 0.92$ | $6.4 \times 10^2$ | this work |
| $Me_3CO^\bullet$ | $8.69 \pm 0.46$ | $2.64 \pm 0.62$ | $5.7 \times 10^6$ | 18 |
| $Cl_3C^\bullet$ | 8.62 | 8.08 | $1.9 \times 10^2$ | 19 |

of $1.8 \times 10^3$ $M^{-1}$ $s^{-1}$ that can be calculated from the neophyl data in Table I.

The values of *k* in Table I are absolute rate constants and measure the overall (or molecular) reactivity of substrates, regardless of the site or mechanism of reaction. Thus, on the basis of kinetic studies it has been estimated that the attack of *tert*-butoxyl radicals on triethylsilane occurs in about 80% of the cases at the Si–H moiety and 20% at the ethyl groups at ambient temperature.[18,23] In order to investigate the regioselectivity for the reaction of a primary alkyl radical with $Et_3SiH$, we first measured the rate constant for the reaction of neophyl radical with $Et_3SiD$ relative to neophyl rearrangement and found it to be $k_r/k = 9.72 \pm 0.83$ at 403 K (detailed results of this experiment are also available as supplementary material). A value of $k_r/k = 13$ at 393 K has previously been obtained from a single measurement by the same procedure.[6] Taking $k_r = 1.38 \times 10^5$ $s^{-1}$ at 403 K from ref 12 we calculated $k = 1.42 \times 10^4$ $M^{-1}$ $s^{-1}$. Then, the crude products were analyzed by mass spectrometry to determine the isotopic distribution. From the EI mass spectrum recorded by GC/MS analysis of the reaction mixture, the relative amounts of $PhCMe_2CH_3/PhCMe_2CH_2D = 57/43$ and $PhCH_2C(H)Me_2/PhCH_2C(D)Me_2 = 48/52$ were determined by measuring the relative abundance of the corresponding $M^{\bullet+}$ and $(M + 1)^{\bullet+}$ ions. Taking $k = k_{Et} + k_{SiD} = 1.42 \times {}^{14}$ $M^{-1}$ $s^{-1}$ and $k_{Et}/k_{SiD} = 1.33$ we calculated $k_{SiD} = 6.1 \times 10^3$ $M^{-1}$ $s^{-1}$, $k_{Et} = 8.1 \times 10^3$ $M^{-1}$ $s^{-1}$ at 403 K, where $k_{SiD}$ and $k_{Et}$ are the rate constants for D atom abstraction and H atom abstraction from the ethyl groups, respectively. Futhermore, taking from the neophyl data in Table I $k = k_{Et} + k_{SiH} = 2.15 \times 10^4$ $M^{-1}$ $s^{-1}$ at 403 K we calculated $k_{SiH} = 13.4 \times 10^3$ $M^{-1}$ $s^{-1}$, where $k_{SiH}$ is the rate constant for H atom abstraction from the SiH moiety. It is worth mentioning that the deuterium kinetic isotope effect for the reaction of primary alkyl radical with $Et_3SiH$, i.e., $k_{SiH}/k_{SiD}$, is found to be 2.2 (at 403 K) which is in line with the value of 2.3 for $(Me_3Si)_3SiH$[24] and $Bu_3SnH$[14] at 363 and 330 K, respectively.

Summarizing, the attack of primary alkyl radicals in $Et_3SiD$ occurs in about 40% of the cases at the SiD moiety and 60% at the ethyl groups, whereas on $Et_3SiH$ it occurs in about 60% of the cases at the SiH moiety and 40% at the ethyl groups at 403 K.

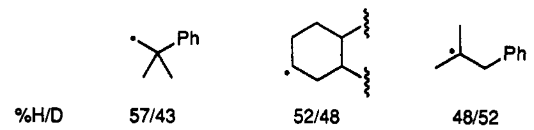
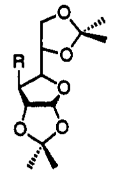
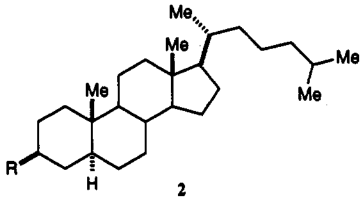


**Figure 1.**



1

a: R = OH
b: R = OC(S)SMe
c: R = OC(S)OAr
d: R = OC(S)OPh
e: R = H



2

a: R = OH
b: R = OC(S)OAr
c: R = OC(S)OPh
d: R = H

**Barton's Approach.** In Barton's approach, the secondary alcohols **1a** and **2a** were transformed into suitable thiocarbonyl derivatives (cf. **1b**, **1c**, and **2b**) and then reacted with $Et_3SiH$ using dibenzoyl peroxide as initiator. The use of the reducing agent $Et_3SiH$ as a solvent and the need of very large quantities of dibenzoyl peroxide as radical initiator indicate that the reaction is not a *normal* chain process. We applied this experimental procedure to the reduction of phenyl thiocarbonates **1d** and **2c**. In agreement with Barton et al.,[10] the deoxygenating products **1e** and **2d** were formed in 86% and 91%, respectively. By replacing $Et_3SiH$ with $Et_3SiD$, the reductions were still efficient (85–90% yield), but the incorporation of H atoms was substantial. In fact, GC/MS analysis of the reaction mixture as well as of isolated products indicates that the deuterium incorporations were 56% and 48% for **1d** and **2c**, respectively, in agreement with our kinetic observations. Consequently, eq 3, being an important step in the reductions of thiocarbonates, should be included in the mechanism proposed by Barton et al.[10]

$$R^\bullet + Et_3SiD \longrightarrow RH + \underset{\textbf{3}}{\left\{\begin{array}{l} Et_2Si(D)\dot{C}HCH_3 \\ Et_2Si(D)CH_2\dot{C}H_2 \end{array}\right\}} \qquad (3)$$

Figure 1 shows that the %D incorporation increases through the series primary, secondary, and tertiary alkyl radicals. This trend probably arises from the different enthalpies of reaction. However, polar effects should also play some role because the secondary alkyl radicals derived from **1** and **2** behave slightly differently, the latter being more nucleophilic than the former.[25]

But what is the fate of carbon-centered radicals **3** produced from eq 3? Presumably radicals **3** either abstract D from $Et_3SiD$ to regenerate the silyl radical or add to the thiocarbonyl moiety for an alternative to Barton's chain propagation. To throw some light on this, we tried to reduce **1d** and **2c** under Barton's reaction conditions, using $Et_4Si$ instead of $Et_3SiH$. Following a normal workup we were able to isolate **1e** and **1d** in 38% and 20%, respectively.

## Conclusions

Our results, which are inconsistent with the mechanism proposed by Barton et al.,[10] indicate that the forced reduction of thionoesters by $Et_3SiH$ is not a common chain process and that the propagation steps are

$$ROC(S)OPh + X^\bullet \rightarrow R^\bullet + XSC(O)OPh \qquad (4)$$

$$R^\bullet + Et_3SiH \rightarrow RH + X^\bullet \qquad (5)$$

where $X^\bullet$ represents a number of radicals. The appearance

---

[23] It is worth mentioning that the relative reactivity of $\alpha$- and $\beta$-hydrogen atoms of the ethyl moiety in $Et_4Si$ toward *tert*-butoxyl radicals is 4:1 (per hydrogen atom). Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208.

[24] Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399.

[25] (a) Minisci, F.; Fontana, F.; Vismara, E. *Gazz. Chim. Ital.*, in press. (b) Vismara, E.; Donna, A.; Marchiandi, M.; Minisci, F.; Naggi, A.; Pastori, N.; Torri, G. *J. Org. Chem.*, in press. We thank Prof. F. Minisci for kindly sending us a copy of these articles prior to publication.

of $Et_3SiH$ as an efficient radical reducing agent of only thionoesters is probably due to the fact that the variety of involved radicals (i.e. $X^\bullet$ and those derived from the decomposition of benzoyl peroxide[26]) add fast to the thiocarbonyl moiety.

## Experimental Section

**Materials.** Neophyl bromide,[27] di-*tert*-butyl hyponitrite,[28] and phenyl thiocarbonates[29] **1d** and **2c** were prepared following literature procedures. $Et_3SiD$ was obtained from the corresponding silyl chloride with $LiAlD_4$. All other materials were commercially available and used as received.

**General Procedure for Kinetic Measurement.** 1,3-Di-*tert*-butylbenzene containing a small amount of nonane as an internal GC standard was used as solvent. Triethylsilane and the neophyl bromide was 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 ampules and were thermolyzed. 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 °C using a Varian 3300 chromatograph. The hydrocarbon products of interest were identified by comparison of their retention times with authentic material.

**GC/MS Studies.** The measurements were performed using a Hewlett-Packard GC5890 (Series II) coupled to a Hewlett-Packard mass selective detector Model 5971A. Analyses were obtained via a splitless injection on a 25-m × 0.2-mm cross-linked 5% phenylsilicone capillary column (HP-5). The crude or isolated products were identified by comparison with authentic samples of the hydrocarbons. Single ion monitoring (SIM) mode was used to determine isotopic distribution (% H/D incorporation) in the products, focusing on $M^{\bullet+}$ and $(M + 1)^{\bullet+}$ ions.

**Reduction of Phenyl Thiocarbonates.** A ca. 0.3 M solution of a thiocarbonate in the appropriate silane was degassed. Then the solution was heated at ca. 110 °C for 2–3 h and treated with dibenzoyl peroxide at 30-min intervals (total 1 equiv). Then the solvent was evaporated in vacuum and the desired product isolated by column chromatography on silica.

**Acknowledgment.** We thank Prof. D. H. R. Barton for kindly sending us a copy of his article prior to publication and for teasing us on the subject "organosilanes as radical-based reducing agents in synthesis", in the lack of which we would never have started this work. We wish to express our gratitide to Mr. B. Ballestri and Mr. A. Guerrini for their technical assistance and to Prof. F. Minisci for helpful discussions. We thank the Progetto Finalizzato Chimica Fine II (CNR, Rome) for financial support.

**Supplementary Material Available:** Tables II–IV giving detailed product ratio of kinetics (4 pages). This material is contained in 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.

---

[26] Coppa, F.; Fontana, F.; Minisci, F.; Pianese, G.; Tortoreto, P.; Zhao, L. *Tetrahedron Lett.* **1992**, *33*, 687.

[27] Fainberg, A. H.; Winstein, J. *J. Am. Chem. Soc.* **1956**, *78*, 2763.

[28] Mendenhall, G. D. *Tetrahedron Lett.* **1983**, *24*, 451.

[29] Robins, M. J.; Wilson, J. S.; Hansske, F. *J. Am. Chem. Soc.* **1983**, *105*, 4059. Robins, M. J.; Wilson, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 933.