Hydrosilylation of C−C Multiple Bonds Using (Me₃Si)₃SiH in Water. Comparative Study of the Radical Initiation Step

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The classical radical-based hydrosilylation reaction of organic compounds bearing C−C multiple bonds is usually carried out in organic solvents and is herein presented in water with both organic solvent-soluble and water-soluble substrates. Different initiation methods to accomplish the radical-induced hydrosilylation reaction of C−C multiple bonds in water with (Me₃Si)₃SiH are presented. In the thermal decomposition of azo compounds, the system comprising substrate, silane, and azo-initiator (ACCN) mixed in aqueous medium at 100 °C worked well for both hydrophilic and hydrophobic substrates, with the only variation that the amphiphilic thiol HOCH₂CH₂SH was also needed in the case of the water-soluble compounds. Dioxygen initiation is shown to afford excellent yields of hydrosilylated products derived from substrates bearing C−C triple bonds and moderate to low yields of hydrosilylated products derived from C−C double-bonded compounds in water. Photochemical initiation in the absence of a chemical radical precursor other than the silane is also found to be a very efficient and convenient method to induce the hydrosilylation reaction of both C−C double and triple bonds of organic compounds (hydrophilic and hydrophobic substrates) with (Me₃Si)₃SiH in water. These three alternative radical-based methodologies studied in water are confronted.

Introduction

The radical-based hydrosilylation of carbon−carbon multiple bonds by (Me₃Si)₃SiH is an important class of reactions.[1,2] The initially generated (Me₃Si)₃Si• radical adds to the double or triple bond to give a radical adduct, which then abstracts a hydrogen from the starting silane and affords the addition product, together with "fresh" (Me₃Si)₃Si• radicals to continue the chain. The applications of this class of reactions span from the synthesis of organosilane compounds (including sequential radical transformations) to the synthetic architecture of monolayers. Indeed, radical reactions have been found to be the most convenient strategy for achieving organic modifications of hydrogen-terminated silicon surfaces among the several existing methodologies.[3] The two flat surfaces H−Si(111) and H−Si(100)-2×1 resemble (Me₃Si)₃SiH in that three silicon atoms are attached at the SiH moieties, and therefore, it is not surprising that several (Me₃Si)₃SiH reactions have been adopted and applied to surfaces and that mechanistic schemes are often proposed in analogy with (Me₃Si)₃SiH radical chemistry.[4,5]

The radical-based hydrosilylation reactions are generally performed in organic solvents,[6,7] in water,[8] or under solvent-free conditions.[5,9] More recently, these reactions are also performed in continuous-flow microreactors.[10] In these radical chain processes, the initial silyl radicals are generated by some initiation. The most popular thermal initiator is 2,2′-azobisisobutyronitrile (AIBN), with a half-life of 1 h at 81 °C, generating the incipient radicals that commence the radical chain reaction.[6,10] Other azo-compounds are used from time to time[8,11] as well as the thermal decomposition of di-*tert*-butylperoxide[12] depending on the reaction conditions. Et₃B in the presence of very small amounts of oxygen is an excellent initiator for low-temperature reactions (down to −78 °C).[6,7] Also air-initiated reactions have recently been reported.[5,9]

Hydrosilylation of monosubstituted and *gem*-disubstituted olefins occurs with high regioselectivity (*anti*-Markovnikov) in the case of both electron-rich and electron-poor olefins.[6] For *cis* or *trans* disubstituted double bonds, hydrosilylation is still an efficient process, although it requires slightly longer

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(1) Chatgilialoglu, C. *Organosilanes in Radical Chemistry*; Wiley: Chichester (UK), 2004.
(2) Chatgilialoglu, C. *Chem.—Eur. J.* **2008**, *14*, 2310–2320. Chatgilialoglu, C.; Timokhin, V. I. *Adv. Organomet. Chem.* **2008**, *57*, 117–181. Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188–194.
(3) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271–1308. Wayner, D. D. M.; Wolkow, R. A. *J. Chem. Soc., Perkin Trans. 2* **2002**, *23*, 34.
(4) Wang, D.; Buriak, J. M. *Langmuir* **2006**, *22*, 6214–6221.

(5) Liu, Y.; Yamazaki, S.; Yamabe, S. *J. Org. Chem.* **2005**, *70*, 556–561. Liu, Y.; Yamazaki, S.; Yamabe, S.; Nakato, Y. *J. Mater. Chem.* **2005**, *15*, 4906–4913. Liu, Y.; Yamazaki, S.; Izuhara, S. *J. Organomet. Chem.* **2006**, *691*, 5821–5836.
(6) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994–4000.
(7) Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356–2364.
(8) Postigo, A.; Kopsov, S.; Ferreri, C.; Chatgilialoglu, C. *Org. Lett.* **2007**, *9*, 5159–5162.
(9) Wang, J.; Zhu, Z.; Huang, W.; Deng, M.; Zhou, X. *J. Organomet. Chem.* **2008**, *693*, 2188–2192.
(10) Odedra, A.; Geyer, K.; Gustafsson, T.; Gilmour, R.; Seeberger, P. H. *Chem. Commun.* **2008**, *3025*, 3027.
(11) Yasuda, H.; Uenoyama, Y.; Nobuta, O.; Kobayashi, S.; Ryu, I. *Tetrahedron Lett.* **2008**, *49*, 367–370.
(12) Naka, A.; Ohnishi, H.; Ohshita, J.; Ikadai, J.; Kunai, A.; Ishikawa, M. *Organometallics* **2005**, *24*, 5356–5363.

reaction times and an activating substituent.[6] No hydrosilylation product has been observed with 1,2-dialkyl-substituted olefins due to the reversible addition of $(Me_3Si)_3Si^\bullet$ radical to the double bonds.[13] Rate constants for the reaction of $(Me_3Si)_3Si^\bullet$ radicals with a variety of monosubstituted olefins have been measured by laser flash photolysis techniques.[14,15] Variants of hydrosilylations, in which the intermediate silyl adducts undergo β-elimination of sulfonyl or thiyl radicals, are also reported.[16,17] The addition of $(Me_3Si)_3SiH$ to a number of monosubstituted acetylenes is also highly regioselective (*anti*-Markovnikov) and gives terminal $(Me_3Si)_3Si$-substituted alkenes in good yields.[5,6,7] High *cis* or *trans* stereoselectivity is also observed, depending on the nature of the substituents at the acetylenic moiety.

$(Me_3Si)_3SiH$ is not soluble in water and does not suffer from any significant reaction with water at 100 °C for a few hours.[18] This observation motivated our interest in applying it to radical reactions in water. In our recent communication,[8] the reduction of hydrophobic substrates was successfully carried out in good yields, using $(Me_3Si)_3SiH$ and 1,1'-azobis(cyclohexanecarbonitrile) (ACCN) as the initiator at 100 °C. This procedure does not work with water-soluble substrates; however when a catalytic amount of the amphiphilic 2-mercaptoethanol is added to $(Me_3Si)_3SiH$, it becomes a very efficient system for the reduction of different substrates. A few hydrosilylation reactions were also found to proceed effectively.[8] In the present article, we report an extension of the hydrosilylation of carbon–carbon double and triple bonds by $(Me_3Si)_3SiH$ in water, investigating also various methods of radical initiations, as well as the competition reaction with the *gem*-dichlorocyclopropane moiety reduction. Our findings are meant to contribute to a full evaluation on the protocols of hydrosilylation in aqueous solutions.[19]

Results and Discussion

Methods of Radical Initiation in Water. The water-insoluble radical initiator ACCN (half-life of 2.33 h at 100 °C) has been found to give the best performance for both hydrophobic and hydrophilic substrates in the initial study,[8,18] and this trend has been confirmed by the present results. The procedure is the following: In a 5 mL Wheaton vial, provided with a stir bar, a heterogeneous aqueous mixture of the hydrophobic substrate (10 mM), $(Me_3Si)_3SiH$ (1.2–2.0 equiv), and ACCN (0.3 equiv) is flushed with Ar for 10 min before heating at 100 °C for 4 h or otherwise indicated. For hydrophilic substrates, the procedure varies slightly, now including the amphiphilic thiol $HOCH_2CH_2SH$ (0.3 equiv). The isolation and purification of products are described in the Experimental Section.

The high temperature needed for the decomposition of the initiator (ACCN, up to 100 °C) precludes the treatment of thermally labile substrates and compromises the stability of

products. We therefore embarked on exploring other different and milder radical initiating techniques, such as dioxygen or photochemical initiation, to be used for the aqueous methodology.

A balloon filled with pure oxygen connected to the vessel through a needle deeply immersed in the solution allowed dioxygen to be introduced. We carried out the dioxygen-initiated radical-induced hydrosilylations of lipophilic substrates in Ar-degassed water by adding subsequently $(Me_3Si)_3SiH$ (6×10^{-5} mol) and the substrate (5×10^{-5} mol). The vessel was tight sealed, connected with a balloon filled with 99.99% dioxygen, and vigorously stirred at 20 °C. For hydrophilic substrates, $HOCH_2CH_2SH$ (0.3 equiv) was employed as the chain-propagating agent.

The hydrosilylation reactions in water were also initiated directly with light (low-pressure Hg lamp, 254 nm) in the absence of a radical chemical precursor (e.g., peroxide), where most of the light was absorbed by $(Me_3Si)_3SiH$. Ar-degassed water (3 mL) was placed in a quartz cell provided with a stir bar, with subsequent addition of $(Me_3Si)_3SiH$ (3×10^{-5} mol) and the substrate (3×10^{-5} mol) by syringe. The cell is mounted on a stir plate at a 1 cm distance from the lamp and stirred vigorously throughout the irradiation time (1.5–2 h). The temperature is controlled thermostatically at 20 °C.

Hydrosilylation of Alkenes. The reaction of $(Me_3Si)_3SiH$ with various alkenes (reaction 1) was studied under the various methods described above, and the yields of hydrosilylation products are reported in Table 1.

$$(Me_3Si)_3SiH \ + \ \diagup\!\!\!\diagdown R \ \xrightarrow{H_2O} \ (Me_3Si)_3Si\diagdown\!\!\!\diagup\!\!\!\diagdown R \quad (1)$$
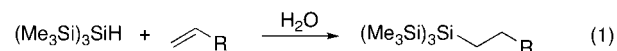
Column 3 shows the yields of hydrosilylated products obtained by thermal decomposition of ACCN as the initiation, and all of them are high. Thus, the hydrosilylated product derived from 1-octen-3-ol is obtained almost quantitatively, as well as the hydrosilylated product derived from 2,3-dihydrofuran (95%). High yields of hydrosilylation are obtained from allylacetate (isolated in 85% yield). When the water-soluble vinyl ethylene glycol ether is treated with $(Me_3Si)_3SiH$ in the presence of a $HOCH_2CH_2SH$ under ACCN initiation in water, the corresponding hydrosilylated product (organic solvent soluble) is obtained in 95% yield (entry 4). In the absence of the thiol, poor yields of hydrosilylated product are obtained.

The hydrosilylation yield of alkenes, initiated by dioxygen as described above, is very sensitive to the substrate employed. Thus, from Table 1, column 4, the hydrophobic 1-octen-3-ol (entry 1) afforded the corresponding hydrosilylated product in water in a 72% yield after 24 h, although the conversion of the starting material is only 50%.[20] Analogously, 2,3-dihydrofuran (entry 2) and allyl acetate (entry 3) afforded the corresponding hydrosilylated products in 65–67% yield, the conversion of starting material being 80%. The reaction of the water-soluble vinyl ethylene glycol ether (entry 4) with $(Me_3Si)_3SiH$, under dioxygen initiation, in the absence or presence of $HOCH_2CH_2SH$, did not lead to any product.

From Table 1, column 5, it is evident that the hydrosilylation reactions of alkenes initiated by light proceeded very efficiently in water, the hydrosilylation products being obtained almost quantitatively with nearly complete substrate consumption. At

(13) Chatgilialoglu, C.; Ballestri, M.; Ferreri, C.; Vecchi, D. *J. Org. Chem.* **1995**, *60*, 3826–3831.

(14) Ballestri, M.; Chatgilialoglu, C.; Clark, K. B.; Griller, D.; Giese, B.; Kopping, B. *J. Org. Chem.* **1991**, *56*, 678–683.

(15) Lalevée, J.; Allonas, X.; Fouassier, J. P. *J. Org. Chem.* **2007**, *72*, 6434–6439.

(16) Wnuk, S. F.; Garcia, P. I.; Wang, Z. *Org. Lett.* **2004**, *6*, 2047–2049.

(17) Chatgilialoglu, C.; Ballestri, M.; Vecchi, D.; Curran, D. P. *Tetrahedron Lett.* **1996**, *37*, 6383–6386.

(18) Postigo, A.; Ferreri, C.; Navacchia, M. L.; Chatgilialoglu, C. *Synlett.* **2005**, 2854–2856.

(19) For a recent review "on water" reactions, see: Chanda, A.; Fokin, V. V. *Chem. Rev.* **2009**, *109*, 725–748.

(20) We also attempted the hydrosilylation of 1-octen-3-ol in the absence of solvent and in the presence of air. We allowed the neat mixture (50×10^{-5} mol of substrate and 50×10^{-5} mol of silane) to stir for 48 h in an open vessel. After the reaction time elapsed, no hydrosilylation product is observed, and the susbtrate is recovered unaltered.

Table 1. Hydrosilylation Reactions of C−C Double Bonds: Organic Solvent-Soluble Substrates and Hydrophilic Substrates (10 mM) in Water with (Me₃Si)₃SiH (12 mM) under Different Initiation Conditions

| Entry	Substrate	ACCN (100 °C, 4h) Yield, %	O₂-initiated Yield, %	hv (254 nm) Yield, %
1	(1-octen-3-ol, OH)	99	72[a]	99
2	(2,3-dihydrofuran)	95	67[b]	99
3	(allyl acetate)	85, 99[a]	65[b]	85, 95[a]
4[c]	(vinyl ethylene glycol ether, O, OH)	95	–	99

[a] Yield based on 50% starting material consumption. [b] Yield based on 80% starting material consumption. [c] HOCH₂CH₂SH (0.3 equiv) was added as chain carrier.

the working concentrations, most of the light (254 nm) is absorbed by (Me₃Si)₃SiH. Disilanes are known to undergo a variety of fragmentation reactions under photolysis depending on the nature of the substituents.[1,2] The most common reaction is the extrusion of silylenes rather than formation of radicals by Si−Si bond homolysis. UV irradiation of (Me₃Si)₃SiX is reported to generate silylenes.[21,22] We suggest that either a minor photolytic path accounts for the formation of silyl radical that initiates the radical chain hydrosilylation or, unlike the photolysis of silanes in organic solvents, silyl radical production represents an important deactivating route of the singlet excited state of silanes in water. Under these conditions, the hydrosilylated products derived from 1-octen-3-ol and 2,3-dihydrofuran were obtained quantitatively (entries 1 and 2). A high hydrosilylation yield is also obtained from allylacetate in water (entry 3). When the water-soluble vinyl ethylene glycol ether is treated with (Me₃Si)₃SiH in the presence of a HOCH₂CH₂SH under the same conditions, the corresponding hydrosilylated product (organic solvent soluble) was obtained quantitatively (entry 4). In the absence of the thiol, poor yields of hydrosilylated product are obtained. This yield should be compared with that for the reaction in the presence of dioxygen in water, where no hydrosilylation product derived from the water-soluble vinyl ethylene glycol ether is observed (entry 4, column 4).

Hydrosilylation of Alkenes Containing a 1,1-Dichlorocyclopropane Moiety. We then proceeded to examine the reaction of a series of alkenyl-substituted 1,1-dichlorocyclopropanes with (Me₃Si)₃SiH in water, in order to explore the competition of reduction and hydrosilylation and deem whether the different initiation methods have bearing on this competition.

We first focused on the 1,1-dichlorocyclopropane derivatives without alkenyl substituents. Knowledge on the reduction of *gem*-dichlorides by (Me₃Si)₃SiH is limited to some stereoselective studies in organic solvents.[23] We therefore considered reduction of *gem*-dichlorides **1a** and **1b** in water (reaction 2). Reduction of compound **1a** or **1b** (10 mM) with (Me₃Si)₃SiH (12 mM) and ACCN (3 mM) in Wheaton vials (5 mL total

volume) warmed at 100 °C for 4 h proceeded smoothly to afford the corresponding monochloride derivatives, in quantitative yields based on the recovered starting materials, as a diastereoisomeric mixture **2/3** = 1.7:1 for both cases. The outcome of these reactions is probably due to influence of the substituents on the rate of the cyclopropyl radical and on the shielding of the two faces of the cyclopropyl ring.[23,24]

$$1a: R_1 = C_5H_{11}, R_2 = H \qquad 2 \qquad 3$$
$$1b: R_1 = CH_3, R_2 = Ph$$
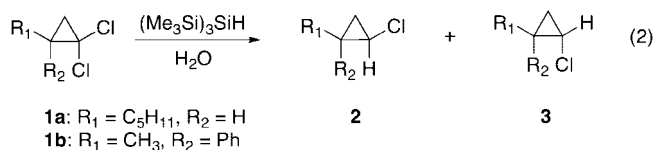
Next we considered the reduction of compound **4** in water, a cyclopropane ring bearing allyloxymethyl and *gem*-dichloride substituents. A mixture of compound **4** (10 mM) with (Me₃Si)₃SiH (12 mM) and ACCN (3 mM) in 5 mL of deareated water in Wheaton vials was warmed at 70 °C for 1 h. Workup of the reaction afforded the hydrosilylated product **5** with retention of both chlorine atoms (Scheme 1). Prolonged reaction times showed the formation of monochloride **6**. Figure 1 shows the substrate transformation during the course of the reaction followed by GC analysis, indicating the formation of the addition product **5** and its decay due to the reduction with formation of the final monochloride diastereoisomeric mixture of **6**. Indeed, quantitative reduction to monochloride **6** (99% yield) can be obtained in 4 h at 70 °C, by using **5** (10 mM), (Me₃Si)₃SiH (20 mM), and ACCN (3 mM) as initiator. The *cis/trans* = 1.5:1 isomeric mixture of **6** was determined after separation by flash chromatography and NMR analysis.
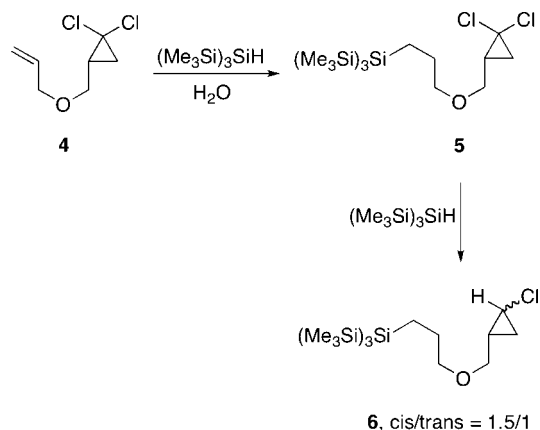
It is worth mentioning that the hydrosilylation of compound **4** with (Me₃Si)₃SiH was also carried out under the dioxygen initiation or photostimulation conditions reported above. In the former case, the starting material conversion was very low, with formation of **5** as expected, whereas in the latter a

(21) Chen, Y. S.; Gaspar, P. P. *Organometallics* **1982**, *1*, 1410–1412.
(22) Brook, M. A.; Balduzzi, S.; Mohamed, M.; Gottardo, C. *Tetrahedron* **1999**, *55*, 10027–10040.

(23) Apeloig, Y.; Nakash, M. *J. Am. Chem. Soc.* **1994**, *116*, 10781–10782.
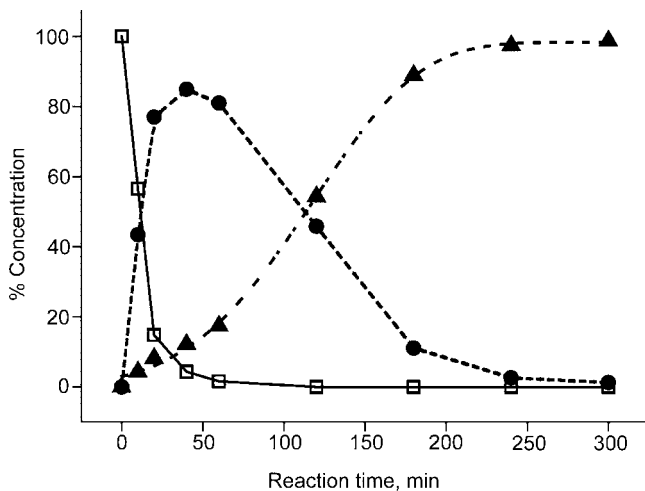(24) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*; VCH: Weinheim, 1995.

Scheme 1. Reaction of *gem*-Dichloride 4 with (Me₃Si)₃SiH in Water

Scheme 2. Hydrosilylation of 1,1-Dichloro-2-vinylcyclo-propane in Water by (Me₃Si)₃SiH

lene, 1-phenylacetylene, and propiolic acid) were treated with (Me₃Si)₃SiH under the above reaction conditions and yielded the respective alkenes stereoselectively in high yields (reaction 3). Normally *Z*-alkenes are formed. The results are summarized in Table 2. It is worth underlining that the moderate though encouraging oxygen-initiated hydrosilylation reaction yields obtained from substituted alkenes in water contrast with those obtained with alkynes, where the results are excellent.
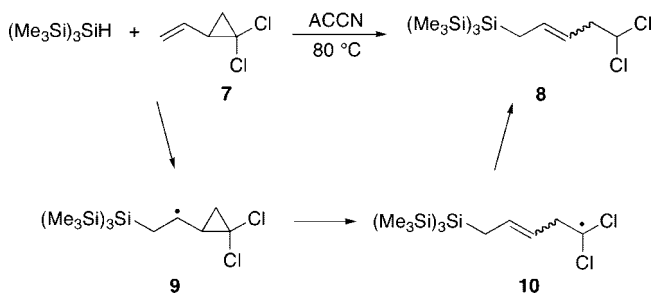
mixture of product **5** and its monochlorinated derivative (*cis/trans* = 1.5:1) was obtained in a relative 39:61 ratio with total consumption of starting material. These results confirm that the photolysis of (Me₃Si)₃SiH at 254 nm is an effective radical initiation process in water as the solvent.

When 1,1-dichloro-2-vinylcyclopropane **7** (10 mM) is made to react with (Me₃Si)₃SiH (4 mM) and ACCN (3 mM) in 5 mL of water in Wheaton vials at 80 °C for 1 h, the hydrosilylation products **8** are obtained as a mixture of geometric isomers, in an 87:13 *trans/cis* ratio, isolated by flash chromatography with pentane as the eluent (R_f = 0.78 in 8:1 pentane/diethyl ether). Under such conditions, the ring-opening product was obtained in a 60% conversion from 1,1-dichloro-2-vinylcyclopropane and 99% yield considering the recovery of the starting material (Scheme 2). It was possible to proceed with a further reduction of the chlorine atoms in compound **8**, by using an increased amount of (Me₃Si)₃SiH and ACCN as initiator (ratio substrate:silane:initiator = 1:2:0.3) and prolonged reaction time (4 h). The reaction mechanism of this reaction is depicted in Scheme 2, which involves addition of (Me₃Si)₃Si• radical to the terminal olefin to give **9**, which undergoes ring-opening to form radical **10**.[25] Hydrogen abstraction from the silane gives **8** and (Me₃Si)₃Si• radical, thus completing the cycle of this chain reaction.
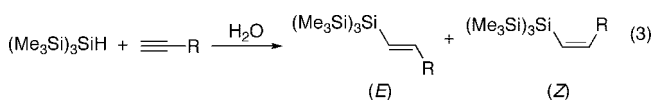
Hydrosilylation of Alkynes. Alkynes also react with (Me₃Si)₃SiH in a radical chain reaction in water as solvent. A series of monosubstituted alkynes (1-octyne, 1-cyclohexylacety-

$$(Me_3Si)_3SiH + \;\equiv\!\!-R \xrightarrow{H_2O} \underset{(E)}{(Me_3Si)_3Si\diagup\!\!\diagdown_R} + \underset{(Z)}{(Me_3Si)_3Si\diagdown\!\!\diagup R} \quad (3)$$

When water-insoluble alkynes are made to react with (Me₃Si)₃SiH under ACCN initiation conditions, the corresponding hydrosilylated alkenes were obtained isolated in >90% yield (column 3, entries 1−3). The hydrosilylation of water-soluble propiolic acid initiated by ACCN was also tested under similar reaction conditions, although in this case, HOCH₂CH₂SH is added as the chain carrier. The reaction proceeded affording the hydrosilylated alkene in a 95% yield (column 3, entry 4). Comparison of these data with the analogous reactions carried out in toluene at 80−90 °C and AIBN as initiator[6] shows not only better product yields but also a higher stereoselectivity in favor of the *Z* isomer. For example, the *Z:E* ratio for 1-cyclohexylacetylene varies from 45:55 in toluene (80 °C)[6] to 74:26 in water (100 °C). Unconjugated vinyl radicals are known to be sp² hybridized and to invert with a very low barrier (eq 4).[24] The higher stereoselectivity in favor of the *Z* isomer, under our experimental conditions, suggests that additional factors are playing a role in water. It could be hypothesized that the hindrance of approach of the bulky silane to the radicals may also be influenced by the organization of the organic material dispersed in water.
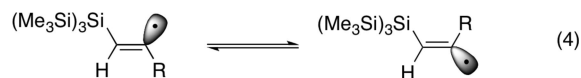
$$(4)$$

When water-insoluble alkynes are made to react with (Me₃Si)₃SiH under dioxygen initiation at 22 °C, the corresponding hydrosilylated alkenes were obtained at even higher yields and, more importantly, the hydrosilylation products were exclusively in the *Z* geometrical configuration (column 4, entries 1−3). The hydrosilylation reaction of water-soluble propiolic acid also occurs smoothly in the presence of a thiol, affording the *Z*-alkene in nearly quantitative yield (column 4, entry 4). Comparison of these data with the analogous reactions carried out in toluene with Et₃B/O₂ as initiator at 25 °C, or in benzene with Et₃B as initiator at room temperature, shows not only better yields but also higher stereoselectivity in favor of the *Z* isomer. For example, the *Z:E* ratio for 1-cyclohexylacetylene varies from 96:4 in toluene (25 °C)[6] to >99:1 in water (22 °C) under


Figure 1. Yields of disappearance of starting material **4** (□) and the formation of products **5** (●) and **6** (▲) in water vs reaction time.

Table 2. Hydrosilylation Reactions of C−C Triple Bonds: Organic Solvent-Soluble Substrates and Hydrophilic Substrates (10 mM) in Water with (Me₃Si)₃SiH (12 mM) under Different Initiation Conditions

Entry	Substrate	ACCN (100 °C, 4h) Yield, % (Z:E ratio)	O₂-initiated Yield, % (Z:E ratio)	hv (254 nm) Yield, % (Z:E ratio)
1	≡—CH₂(CH₂)₄CH₃	95 (90:10)[a]	92 (>99:1)	90 (91:9)
2	≡—⬡	90 (74:26)	95 (>99:1)	97 (78:22)
3	≡—◯(phenyl)	93 (70:30)[b]	99 (99:1)	98 (75:25)
4[c]	≡—C(O)OH	95 (99:1)	99 (99:1)	95 (97:3)

[a] Yield based on 75% starting material consumption. [b] In ref 8 the 99:1 ratio is erroneously reported. [c] HOCH₂CH₂SH (0.3 equiv) was added as chain carrier.

dioxygen initiation. The above suggestion that additional factors in water play a role for stereoselectivity is reinforced.

It is worth mentioning that initiation with oxygen does not take place under O₂ purging of the solution, nor with slow, continuous bubbling of O₂ or air. Oxygen or air introduced slowly by syringe-pump techniques resulted in a less efficient initiation of the chain radical reaction. Probably, the slow oxygen addition into the solution with the balloon technique described above allows for sufficient oxygen to be dissolved in the water environment, thus initiating the radical chain (the solubility of oxygen in water is 1.34×10^{-3} M at 22 °C; taking into account that the substrate and (Me₃Si)₃SiH concentrations are ca. 10 times higher, limiting working initiator concentrations could be reached by the methodology). It can be pointed out that a small minor byproduct detected from the oxygen-initiated reactions in water corresponds to a compound detected by mass spectrometry of mass 280 and formula minima $C_9H_{28}SiO_2$ whose structure has been assigned to $(Me_3SiO)_2Si(H)SiMe_3$, arising from the autoxidation of silane. (Me₃Si)₃SiH as a pure material or in solution reacts spontaneously and slowly at ambient temperature with molecular oxygen from air, to form the siloxane.[26] The mechanism of this unusual process has been studied in some detail.[27] Absolute rate constants for the spontaneous reaction of (Me₃Si)₃SiH with molecular oxygen (reaction 5) have been determined to be $\sim 3.5 \times 10^{-5}$ M^{-1} s^{-1} at 70 °C,[27] and theoretical studies elucidated the reaction coordinates.[5]

$$(Me_3Si)_3SiH + O_2 \rightarrow (Me_3Si)_3Si^{\cdot} + HOO^{\cdot} \qquad (5)$$

Table 2 (column 5) also shows that the hydrosilylation of alkynes can successfully be obtained under irradiation conditions. For the hydrosilylation reaction of water-soluble propiolic acid, the adjuvant thiol is necessary. Yields are as good as those obtained by the other procedures. However, lower stereoselectivity in favor of the Z isomer is observed with respect to dioxygen initiation, although the reaction temperatures are very similar. We suggest that Z−E isomerization of products occurs during the reaction course. Although (Me₃Si)₃Si• is able to induce Z−E isomerization of double bonds,[13] it was shown that (Me₃Si)₃Si-subtituted alkenes were not isomerized by (Me₃Si)₃Si• radicals due to steric hindrance of the attack.[7] Hydrosilylated acetylenes have tail absorptions at the irradiation wavelenght (254 nm), and we suggest that a photoisomerization process is responsible for the lower observed stereoselectivity under photoinitiation reactions.

Experimental Section

GC/MS spectra were recorded on 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). Oven program: starting at 50 °C for 5 min, followed by an increase of 5 °C/min up to 250 °C. NMR spectra were recorded on a Varian Mercury instrument at 400 MHz (for ¹H) or 100.6 MHz (for ¹³C) in CDCl₃ as deuterated solvent and referenced with the residual solvent peak at 7.26 ppm in the ¹H NMR spectra and 77.0 ppm in the ¹³C NMR spectra. When necessary, compounds were isolated by flash chromatography performed on silica gel with elution solvents as specified in the text.

1-Octen-3-ol, cyclohexylacetylene, phenylacetylene, 1-octyne, 2,3-dihydrofuran, allylacetate, and tris(trimethylsilyl)silane are commercially available and were used as received from the supplier. Water was obtained from a milli-Q system, and extraction and chromatographic solvents were HPLC-grade. Products from entry 1 (Table 1) and entries 1, 2, 3, and 4 (Table 2) were characterized by standard spectroscopic techniques and compared with spectral data from the literature.[6,8,9,16]

Synthesis of 1,1-Dichlorocyclopropanes. *gem*-Dichlorocyclopropanes have been prepared according to the method of dichlorocarbene addition to alkenes.[28] Briefly, a mixture of the diene (0.1 mol), chloroform (300 mL), and benzyltrimethylammonium chloride (0.04 mmol, 0.0074 g) as a phase-transfer catalyst was prepared in a 1 L three-neck round-bottom flask equipped with a magnetic stirrer and a dropping funnel. Then 50% aqueous NaOH (320 g) was added to the reaction mixture with strong stirring and cooling during 1 h. After additional 2 h stirring at 10 °C, the reaction was stopped,

(25) Gansüer, A.; Pierobon, M. In *Radicals in Organic Synthesis*; Renaud, P.; Sibi, M. P., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 2, pp 207−220.

(26) Chatgilialoglu, C.; Guarini, A.; Guerrini, A.; Seconi, G. *J. Org. Chem.* **1992**, *57*, 2207–2208.

(27) Zaborovskiy, A. B.; Lutsyk, D. S.; Prystansky, R. E.; Kopylets, V. I.; Timokhin, V. I.; Chatgilialoglu, C. *J. Organomet. Chem.* **2004**, *689*, 2912–2919.

(28) Makosza, M.; Wawrazyniewicz, W. *Tetrahedron Lett.* **1969**, 4659–4662.

and the organic phase was separated, washed with water, and dried over anhydrous magnesium sulfate. After solvent evaporation the residue was distilled. The products are obtained as oils. 1,1-Dichloro-2-pentylcyclopropane (**1a**)[29] and 1,1-dichloro-2-methyl-2-phenylcyclopropane (**1b**)[30] were isolated and characterized as described in the literature.

2-(Allyloxymethyl)-1,1-dichlorocyclopropane (4). Bp: 80−82 °C (15 mmHg). ^{1}H NMR, δ: 1.23 (t, J = 7.6 Hz, 1 H), 1.65 (dd, J = 10.6, 7.1 Hz, 1 H), 1.88−1.96 (m, 1 H), 3.53−3.62 (dq, J = 5.8, 7.7 Hz, 2 H), 4.02−4.05 (m, 2 H), 5.20 (dq, J = 10.3, 1.2 Hz, 1 H), 5.25 (dq, J = 17.2, 1.5 Hz, 1 H), 5.92 (m, 1 H). ^{13}C NMR, δ: 24.9, 29.9, 59.8, 69.3, 71.7, 117.3, 134.4. GC/MS, m/z: 181 (M$^+$ + 1, 100), 123, 87, 51. Anal. Calcd for C$_7$H$_{10}$Cl$_2$O: C, 46.43; H, 5.57. Found: C, 46.38; H, 5.55.

1,1-Dichloro-2-vinylcyclopropane (7). Bp: 145 °C. ^{1}H NMR, δ: 1.42 (t, J = 7.7 Hz, 1 H), 1.79 (dd, J = 10.3, 7.1 Hz, 1 H), 2.26−2.32 (m, 1 H), 5.25−5.35 (m, 1 H), 5.51−5.61 (m, 1 H). ^{13}C NMR, δ: 27.6, 33.9, 60.7, 118.9, 133.9. GC/MS, m/z: 136 (M$^+$), 109, 101, 65 (100). Anal. Calcd for C$_5$H$_6$Cl$_2$: C, 43.83; H, 4.41. Found: C, 43.79; H, 4.42.

Hydrosilylation Initiated by Azo Compound Thermal Decomposition. This initiation method has been reported by us previously[8] and described in the text.

Hydrosilylation Initiated by Dioxygen. In a 5 mL Wheaton Reacti-vial provided with a stir bar, 5 mL of water was thoroughly deoxygenated with a fast stream of Ar for 20 min. Five × 10^{-5} mol of substrate and 6 × 10^{-5} mol of TTMSS were added, and the vessel was sealed with a syringe valve. Through the septum, a needle attached to a double balloon filled with pure oxygen was inserted, and the setup is allowed to stir vigorously for 24 h. As the resulting system is airtight, no apparent bubbling of oxygen is observed inside the vial. After the reaction time elapsed, workup consisted of extraction of the resulting turbid aqueous mixture with pentane (thrice), rinse of the pentane layers with water (twice), treatment of the organic phase with anhydrous sodium sulfate, filter, and ulterior addition of a standard (*n*-decane) for quantitation by GC analysis. The silylated products were isolated by silica gel column chromatography, using an HPLC-grade hexane/ethyl acetate mixture as eluent, and characterized by standard spectroscopic techniques.

Hydrosilylation Initiated by Light. In a quartz fluorescence cell provided with a stir bar, 3 mL of water was added and thoroughly deoxygenated with a fast stream of Ar for 20 min. Then 3 × 10^{-5} mol of substrate and 3.6 × 10^{-5} mol of TTMSS were added, and the cell was closed with a Teflon cap. The cell is mounted very near to the low-pressure Hg lamp (254 nm) inside a temperature-controlled setup (20 °C) under vigorous stirring. Irradiation took place for 1.5−2 h. Workup and isolation of products were carried out as previously described.

2-(Tetrahydrofuran-3-yl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (Table 1, entry 2). ^{1}H NMR, δ: 0.19 (s, 27 H); 1.56 (m, 1 H); 1.71 (m, 1 H); 2.12 (m, 1 H); 3.44 (dd, J = 8, 11.5 Hz, 1 H); 3.63 (m, 1 H); 3.81 (dt, J = 2.8, 8.2 Hz, 1 H); 4.05 (t, J = 8 Hz, 1 H). ^{13}C NMR, δ: 1.7, 21.8, 33.0, 68.0, 73.6. GC/MS, m/z: 263 (M$^+$ − 55), 189, 175, 159, 147, 131, 117, 73 (100).

3-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propyl acetate (Table 1, entry 3). ^{1}H NMR, δ: 0.14 (s, 27 H); 0.74 (m, 2 H); 1.66 (m, 2 H); 2.02 (s, 3 H); 3.97 (t, J = 6.7 Hz, 2 H). ^{13}C NMR, δ: 1.0, 3.4, 20.9, 28.0, 67.1, 171.0. GC/MS, m/z: 275 (M$^+$ − 73), 233, 191, 175, 73 (100).

2-(2-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethoxy)ethanol (Table 1, entry 4). The hydrosilylated product derived from vinyl ethylene glycol ether is not water-soluble and was extracted from the crude reaction mixture with pentane (thrice)

and quantified by GC analysis with *n*-decane as the standard. The product was characterized without further purification by standard spectroscopic techniques. ^{1}H NMR, δ: 0.15 (s, 27 H); 1.19 (m, 2 H); 2.20 (br s, 1 H (OH)); 3.52 (m, 4 H); 3.72 (m, 2 H). ^{13}C NMR, δ: 1.05, 9.2, 61.8, 71.1, 71.2. GC/MS, m/z: 235 (M$^+$ − 101), 219, 175, 131, 73 (100).

2-(3-((2,2-Dichlorocyclopropyl)methoxy)propyl-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (5). ^{1}H NMR, δ: 0.16 (s, 27 H), 0.77 (m, 2 H), 1.21−1.28 (m, 2 H), 1.63−1.70 (m, 2 H), 1.87−1.93 (m, 1 H), 3.43 (dt, J = 2.1, 6.8 Hz, 2 H), 3.57 (ddd, J = 5.8, 7.5, 10.9 Hz, 2 H). ^{13}C NMR, δ: 1.1, 3.5, 24.9, 28.9, 29.9, 59.9, 69.8, 73.9. GC/MS, m/z: 355 (M$^+$ − 73), 209, 189, 159, 73 (100). Anal. Calcd for C$_{16}$H$_{38}$Cl$_2$OSi$_4$: C, 44.72; H, 8.91. Found: C, 44.62; H, 8.88.

2-(3-((2-Chlorocyclopropyl)methoxy)propyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6). *cis*-**6**, semisolid (R_f = 0.35; eluent, 2:1 pentane/CHCl$_3$). ^{1}H NMR, δ: 0.17 (s, 27 H), 0.61 (dt, J = 4.2, 6.7 Hz, 1 H), 0.74−0.78 (m, 2 H), 1.12−1.17 (m, 1 H), 1.29−1.37 (m, 1H), 1.67 (m, 2 H), 3.22 (td, J = 4.2, 7.2 Hz, 1 H), 3.43 (t, J = 6.9 Hz, 2 H), 3.53 (dd, J = 7.8, 10.5 Hz, 1 H), 3.64 (dd, J = 5.7, 10.5 Hz, 1 H). ^{13}C NMR, δ: 1.1, 3.4, 13.0, 17.2, 28.9, 32.8, 69.6, 74.0. GC/MS, m/z: 321 (M$^+$ − 73), 209, 189, 175, 73 (100). *trans*-**6**, semisolid (R_f = 0.42; eluent, 2:1 pentane/CHCl$_3$). ^{1}H NMR, δ: 0.16 (s, 27 H), 0.72−0.76 (m, 2 H), 0.89 (dd, J = 6.4, 13.6 Hz, 1 H), 1.00 (m, 1 H), 1.47 (m, 1 H), 1.62 (m, 2 H), 2.90 (m, 1 H), 3.35 (m, 4 H). ^{13}C NMR, δ: 1.1, 3.5, 13.7, 22.1, 28.9, 31.2, 71.1, 73.9. GC/MS, m/z: 321 (M$^+$ − 73), 209, 189, 175, 73 (100).

(5,5-Dichloropent-2-enyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (8). The dichloride **8** was obtained as a mixture of the geometrical isomers in a *trans/cis* ratio of 87:13, by flash chromatography with pentane as the eluent (R_f = 0.78; eluent, 8:1 pentane/diethyl ether), in a 99% yield based on the recovery of the starting material. ^{1}H NMR, δ: 0.16 (s, 27 H), 1.50 (m, 1 H), 1.72−1.77 (m, 2 H), 2.83 (t, J = 6.3 Hz, 2 H, *trans* isomer), 2.93 (t, J = 6.1 Hz, 2 H, *cis* isomer), 5.31 (m, 1 H), 5.63 (t, J = 6.1 Hz, 1 H), 5.71 (m, 1 H). ^{13}C NMR, δ: −1.9, 1.0, 1.7, 1.8, 8.7 (C−Si, *cis*), 13.4 (C−Si, *trans*), 41.1 (C allyl, *trans*), 46,9 (C allyl, *cis*) 73.0, 118.7 (C vinyl, *cis*), 120.1 (C vinyl, *trans*), 134.2 (C vinyl, *cis* (CH$_3$)), 136.1 (C vinyl, *trans*). GC/MS, m/z: 384 (M$^+$), 267, 247, 209, 187, 173, 73 (100). Anal. Calcd for C$_{14}$H$_{34}$Cl$_2$Si$_4$: C, 43.60; H, 8.89. Found: C, 43.72; H, 8.92.

Conclusions

The scope of the hydrosilylation reaction of C−C multiple bonds in water with (Me$_3$Si)$_3$SiH has been expanded from the use of the classical radical initiation through the thermal decomposition of azo compounds to the radical initiation reactions employing photochemical and dioxygen-induced methods. We have shown that the hydrosilylation reactions of alkenes in water by (Me$_3$Si)$_3$SiH can effectively be conducted by both a thermal and a photochemical initiation, rendering the hydrosilylated end-products in high yields. Alkynes are more effectively hydrosilylated in water by (Me$_3$Si)$_3$SiH through dioxygen initiation than alkenes, where this condition affords only moderate to low yields of hydrosilylated alkanes. Remarkably, the hydrosilylation of alkynes in water by (Me$_3$Si)$_3$SiH proceeds with the highest Z-stereoselectivity when the reactions are initiated by dioxygen. The scope of this latter reaction (initiation by dioxygen) is very promising from the point of view of achieving a single geometric isomer or dealing with thermally labile or photolytic substrates/products, where the other initiation techniques compromise such substrate/product stability.

(29) Dzhemilev, U. M.; Gaisin, R. L.; Turchin, A. A.; Khalikova, N. R.; Baikova, I. P.; Tolstikov G. A. *Akad. Nauk. SSSR, Ser. Khim.* **1990**, *39*, 967−974; *Chem. Abstr.* **1990**, *113*, 97058.

(30) McKinney, M. A.; Nagarajan, S. C. *J. Org. Chem.* **1979**, *44*, 2233–2238.