

Different radical initiation techniques of hydrosilylation reactions of multiple bonds in water: thermal and photochemical initiation[†]

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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 hydrophobic and hydrophilic substrates. Thermal and photochemical initiations are used to accomplish the radical-induced hydrosilylation reaction of C—C multiple bonds in water with tris(trimethylsilyl)silane ((Me₃Si)₃SiH). Photochemical radical initiation in the absence of a chemical radical precursor other than the silane is found to be a very efficient and convenient method to induce the hydrosilylation reaction of C—C multiple bonds of organic compounds with (Me₃Si)₃SiH in water. This new alternate radical-based methodology studied in water is confronted with the classical radical thermal initiation of hydrosilylation reactions triggered through the thermal decomposition of azo compounds. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper.

Keywords: photochemical initiation; radical reactions in water; silyl radicals

INTRODUCTION

The importance of the hydrosilylation reactions of multiple bonds has been known for quite some time, and they have been playing a decisive role in surface modifications of several materials, such as porous silicon^[1–4] since the last decade.

The hydrosilylation reaction has been shown to proceed efficiently through the aid of catalysts (Lewis acids), thermal treatment, and radical induced methods.^[5–7] Catalytic hydrosilylation has been exploited profusely, and nowadays has applications in fine and industrial synthetic chemistry.

Radical induced hydrosilylations of organic compounds (in organic solvents) bearing C—C multiple bonds are generally initiated by the thermal decomposition of an azo compound or by photolysis of an organic peroxide, generating the incipient radicals that commence the radical chain reaction. The alkyl radicals (from thermal decomposition of azo compounds or photolysis of alkyl peroxides) abstract hydrogen atoms from the silanes thus producing silyl radicals which in turn add to C—C multiple bonds of organic compounds in organic solvents.^[8]

Mild, metal-free hydrosilylation reactions of olefins have also been carried out employing hydrosilylated cyclohexadienes as radical transfer hydrosilylating agents of multiple bonds in hexane, using AIBN as radical initiator.^[9]

It has also been shown that the radical chain reaction can efficiently be sustained and propagated in solution with the use of a thiol, in a process termed Polarity Reversal Catalysis in which the incipient alkyl radical from the initiator abstracts a hydrogen atom from the thiol generating the thiyl radical which in turn abstracts a hydrogen atom from the silane, thus propagating the chain cycle.^[10]

Catalytic thiols do play a role in the hydrosilylation reactions in water of hydrophilic substrates bearing C—C multiple bonds, as has been shown by us previously.^[10,11] In this previous account, we have shown that the hydrosilylation reactions of organic compounds bearing C—C multiple bonds with (Me₃Si)₃SiH can effectively be performed in water by the thermal decomposition of an azo compound.^[11] Thus, we successfully subjected both lipophilic and hydrophilic C—C multiple-bonded substrates to the hydrosilylation reaction with (Me₃Si)₃SiH in water. In the case of lipophilic C—C multiple-bonded substrates, hydrosilylation in water takes place by the use of (Me₃Si)₃SiH and the thermal decomposition of the azo compound. Conversely, when hydrophilic substrates are employed, an adjuvant thiol to sustain the radical chain reaction is needed. The azo compound employed in both cases is 1,1'-azobis(cyclohexyl)carbonitrile (ACCN) which

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resulted in optimum hydrosilylation reaction yields. The thiol used is the amphiphilic 2-mercaptoethanol. It is worth mentioning the higher *Z* stereoselectivity observed in water *versus* toluene for the hydrosilylation of alkynes with $(\text{Me}_3\text{Si})_3\text{SiH}$. In a more recent study, we have shown how the hydrosilylation of alkynes can take place efficaciously under dioxygen initiation in water, though this initiation technique cannot be used with alkene as substrates.^[12]

From our previous reports, it became apparent that the nature of the reaction medium does not play an important role either in influencing the efficiency of the radical transformation or in the ability to dissolve the reagents. Probably, the radical initiation benefits from the enhanced contact surface of tiny drops containing the reagents (substrate and $(\text{Me}_3\text{Si})_3\text{SiH}$). In the case of water soluble substrates (lower effective concentrations), the amphiphilic thiol supports and enhances the propagating chain reaction.

Though we have been able to establish that the thermal decomposition of ACCN is an excellent method for initiating the hydrosilylation reaction of unsaturated organic compounds in water, the high temperature needed for the decomposition of the initiator (ACCN, 70–100 °C) precludes the treatment of thermally labile substrates and compromises the stability of products. Also, the dioxygen initiation of the radical based hydrosilylation reaction in water, seems only to be effective for alkynes, and not any other C—C multiple bonded substrates. We therefore embarked on exploring other different and milder radical initiating techniques of the well-known radical hydrosilylation reaction with $(\text{Me}_3\text{Si})_3\text{SiH}$, for both alkenes and alkynes, this time performed in water.

RESULTS AND DISCUSSION

Methods of radical initiation in water

Photochemical initiation

We proceeded to attempt the initiation of the hydrosilylation reactions in water 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 were absorbed by $(\text{Me}_3\text{Si})_3\text{SiH}$ (Supporting Information for UV spectrum). To this effect, for all substrates studied, the absorption of $(\text{Me}_3\text{Si})_3\text{SiH}$ (12 mM) at the irradiation wavelength (254 nm) represents *ca.* 95–97% of the total absorption of the mixture (substrate and reagents). Nevertheless, as $(\text{Me}_3\text{Si})_3\text{SiH}$ is not soluble in water, it is assumed that its local droplet-concentration could be much higher, and therefore results in higher local UV-absorbances.

A volume of Ar-degassed water (3 ml) is placed in a quartz cell provided with a stir bar, with subsequent addition of $(\text{Me}_3\text{Si})_3\text{SiH}$ (3×10^{-5} mol) and the substrate (3×10^{-5} mol) by syringe. The cell is mounted on a stir plate very near the lamp (1 cm) and stirred vigorously throughout the irradiation (1.5–2 h). The temperature is controlled thermostatically at 20 °C. At the working concentrations, most of the light (254 nm) is absorbed by $(\text{Me}_3\text{Si})_3\text{SiH}$.

Initiation by thermal decomposition of an azo compound

As mentioned before, the water-insoluble radical initiator 1,1'-azobis(cyclohexanecarbonitrile) (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 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 substrate (10 mM), $(\text{Me}_3\text{Si})_3\text{SiH}$ (1.2–2.0 equiv.) and ACCN (0.3 equiv.) is flushed with Ar for 10 min before heating at 100 °C for 2–4 h or otherwise indicated. After the reaction time elapsed, addition of pentane and extraction, the organic-phase is analyzed. Hydrosilylated products are isolated by silica-gel column chromatography and characterized by standard spectroscopic techniques, or in some cases isolated sufficiently pure to be characterized by standard techniques or compared with authentic samples by spike GC or HPLC injections.

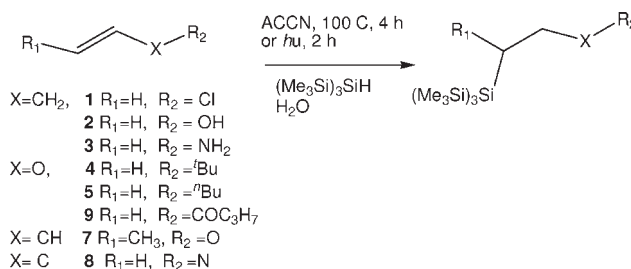
For hydrophilic substrates, the procedure varies slightly, now including the amphiphilic thiol 2-mercaptoethanol: In a 5 ml Wheaton-vial[®], provided with a stir bar, a heterogeneous aqueous mixture of water-soluble starting material (10 mM), $(\text{Me}_3\text{Si})_3\text{SiH}$ (1.2 equiv.), $\text{HOCH}_2\text{CH}_2\text{SH}$ (0.3 equiv.), and ACCN (0.3 equiv.) is flushed with Ar for 10 min before heating at 100 °C (or 70 °C) for 2 h or otherwise indicated. After the reaction time elapsed, addition of hexane, and extraction follows, and the water-phase is analyzed. The reactions of hydrophilic substrates in water have the additional advantage of an easy separation from the silane by-products by partition between water and organic phases.

Hydrosilylation reactions of alkenes in water

In a recent report,^[12] we subjected vinyl-substituted 1,1-dichlorocyclopropane ring systems to the hydrosilylation reaction in water with $(\text{Me}_3\text{Si})_3\text{SiH}$. Employing thermal initiation techniques, hydrosilylation of C=C double bonds is the primary process, and reduction of one of the chlorine atom substituents by $(\text{Me}_3\text{Si})_3\text{Si}$ radicals is obtained under forced reaction conditions.

The reaction of $(\text{Me}_3\text{Si})_3\text{SiH}$ with a new series of alkenes (Scheme 1) in water was studied under the various methods described above, and the yields of hydrosilylation products are reported in Table 1.

In Table 1, column 3, yields of the hydrosilylation products derived from alkenes obtained by ACCN initiation are given for the series of alkenes studied above. Interestingly, the hydrosilylated product derived from hydrophobic 3-chloroprop-1-ene (**1**) is obtained in 65% relative yield (Table 1, column 3, entry 1, product **1a**, 2-(3-chloropropyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane, without chlorine atom reduction). There is also a product derived from the chlorine atom substitution by the $(\text{Me}_3\text{Si})_3\text{Si}$ group (product **1b**, 2-allyl-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane), which is obtained in 35% relative yield.



Scheme 1. Hydrosilylation reactions of alkenes in water by various initiating techniques

Table 1. Hydrosilylation product yields from C—C multiple-bonded organic solvent-soluble substrates and hydrophilic substrates (10 mM) in de-oxygenated water with (Me₃Si)₃SiH (12 mM) under different initiation conditions (ACCN and *hν*)

Entry	Substrate	ACCN (100 °C, 2 h), yield (%)	<i>hν</i> (254 nm), yield (%)
1	3-Chloroprop-1-ene (1)	(1a) 65 ^a (1b) 35 ^a	—
2	Prop-2-en-1-ol (2)	99 ^{b,c}	99 ^{b,c}
3	Prop-2-en-1-amine (3)	(3a) 15 ^{a,c,d} (3b) 85 ^{a,c,d}	(3a) 50 ^{a,c,f} (3b) 50 ^{a,c,f}
4	<i>tert</i> -Butyl vinyl ether (4)	74 ^b	60 ^b
5	<i>n</i> -Butyl vinyl ether (5)	99 ^b	31 ^b
6	Methylenecyclobutane (6)	68 ^b	54 ^b
7	Crotonaldehyde (7)	75 ^{b,c}	90 ^{b,c}
8 ^[14,21]	Acrylonitrile (8)	80 ^b	82 ^b
9	Vinyl butyrate (9)	99 ^b	88 ^b
10 ^[23,23]	3-Chloroprop-1-yne (10)	90 ^{b,e} (Z:E = 50:50)	90 ^{b,e} (Z:E = 50:50)
11 ^[10,11]	Propiolic acid (11)	95 ^{b,c,e} (Z:E = 99:1)	95 ^{b,c,e} (Z:E = 97:3)
12 ^[21–24]	Prop-2-yn-1-ol (12)	90 ^{b,c,e} (Z:E = 75:25)	91 ^{b,c,e} (Z:E = 70:30)

^a Relative product yield.
^b Isolated yield.
^c HOCH₂CH₂SH (0.3 equiv.) was added as chain carrier.
^d Global isolated yield, 75%.
^e Isomer yields obtained from ¹H NMR integration.
^f Global Isolated yield; 65%.

These relative yields were calculated from ¹H NMR integration. The hydrosilylated product derived from *tert*-butyl vinyl ether is also obtained in high yield (substrate **4**, 74%). High yields of hydrosilylation are obtained from *n*-butyl vinyl ether (**5**)^[13] (isolated in 99% yield) in water under ACCN initiation.

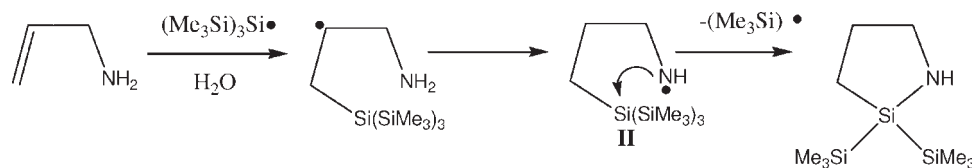
Hydrosilylation products derived from methylenecyclobutane (**6**), acrylonitrile^[13,14] (**8**), and vinyl butyrate (**9**), are obtained in yields ranging from 68% to quantitative, when the reactions are initiated by ACCN (Table 1, column 3, entries 6, 8, and 9).

When the water soluble prop-2-en-1-ol (**2**), prop-2-en-1-amine (**3**), and organic solvent-soluble crotonaldehyde (**7**) are treated with (Me₃Si)₃SiH in the presence of a thiol under ACCN initiation in water, the corresponding hydrosilylated products are obtained in higher than 75% yields (Table 1, column 3, entries 2, 3, and 7). In the absence of the thiol 2-mercaptoethanol, poor yields of hydrosilylated products are obtained. A notable case is that from substrate **3** (isolated global product yield 75%), which renders both a product derived from simple radical hydrosilylation of the C—C double bond (product **3a**, 15% relative yield) and a ring-closed product (**3b**, i.e.: 2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethanamine 85% relative yield). The formation of product **3b** is accounted for in Scheme 2, where the incipient carbon centered radical derived from the addition of the (Me₃Si)₃Si radical to the C—C double bond of the allylamine abstracts a hydrogen atom from the NH₂ group, rendering the

aminyl radical that attacks the Si atom of the ancillary (Me₃Si)₃Si group and undergoes intramolecular radical cyclization.

From Table 1, column 4, the yields of hydrosilylation reactions of alkenes initiated by light in water are reported. Interestingly, the hydrosilylated product derived from hydrophobic 3-chloroprop-1-ene (**1**) is not obtained under photoinitiation. The hydrosilylated product derived from *tert*-butyl vinyl ether (**4**, Table 1, column 4, entry 4) is obtained in moderate yields (60%). The hydrosilylation product from *n*-butyl vinyl ether^[13] is obtained in rather low yield (substrate **5**, hydrosilylated product isolated in 31% yield) in water.

When the water soluble prop-2-en-1-ol (**2**), prop-2-en-1-amine (**3**), and organic solvent-soluble crotonaldehyde (**7**) are treated with (Me₃Si)₃SiH in the presence of a thiol under light initiation in water, the corresponding hydrosilylated products are obtained in high yields (Table 1, column 4, entries 2, 3, and 7). As observed in the thermal initiation, substrate **3** (isolated global product yield 65%), renders both a product derived from simple radical hydrosilylation of the C—C double bond (product **3a**, 50% relative yield) and a ring-closed product (**3b**, i.e.: 2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethanamine 50% relative yield). The formation of product **3b** is accounted for in Scheme 2. This behavior has been observed before in allyl and homoallyl alcohols.^[15] We subjected the open chain hydrosilylated product derived from substrate **3**, that is: 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propan-1-

**Scheme 2.** Proposed mechanism for formation of cyclic product **3b** from the hydrosilylation reaction of allylamine (**3**) in water

amine (**3a**), to photolysis (254 nm) and thermal treatment (ACCN, 100 °C) in water, as indicated in Photochemical Initiation and Initiation by Thermal Decomposition of an Azo Compound Sections. After 2 h reaction, no cyclic product **3b** was formed. This experiment was performed in order to rule out the formation of **3b**, as from a secondary reaction pathway.

In order to give further support to the mechanism suggested in Scheme 2, the isolated open chain product **3a** (4 mM) was treated in water (2 ml) with *tert*-butylhydroperoxide (*t*-BuOOH, 10 mM). The reaction was initiated by light (266 nm). After 40 min-reaction, product **3b** was obtained in *ca.* 45% yield. This simple experiment shows that the aminyl radical **II** (Scheme 2) produced in this latter reaction from H-abstraction from **3a** by *t*-BuO[•] radical, can trigger an intramolecular cyclization with displacement of the Me₃S; group to render product **3b**. Therefore, 1,3-H atom migration to render **II** (Scheme 2) could be suggested to take place along the reaction coordinate. In other works, the intramolecular substitution reaction at silicon, S_Hi mechanism,^[16] has been suggested to yield ring-closure products.^[17]

Notably, the hydrosilylation product derived from substrate **2**, allylic alcohol, only affords an open chain product (99% isolated yield), as opposed to allylamine **3** where products **3a** and **3b** are observed. This difference could be related to the difference in the nucleophilicity of oxygen- and nitrogen-centered radicals in water, as opposed to organic solvents.^[15]

When the reaction is carried out in the absence of the thiol 2-mercaptoethanol, poor yields of hydrosilylated products are obtained from water-soluble substrates **2** and **3**. Water-soluble hydrosilylated products are isolated by mixing the aqueous layer with pentane, the pentane layers discarded (to exclude excess of silane) and the aqueous phase lyophilized. Column chromatography with reverse phase silica is employed to purify the products (ethyl acetate: methanol as eluant) or in some cases, the products are isolated pure enough for spectral characterization (Supplementary Material).

Hydrosilylation products derived from methylenecyclobutane (**6**), acrylonitrile^[13,14] (**8**), and vinyl butyrate (**9**), are obtained in water in yields ranging from 54 to 88%, when the reactions are initiated photochemically (Table 1, column 4, entries 6, 8, and 9).

We suggest that UV-irradiation of (Me₃Si)₃SiH generates silyl radicals from homolysis of the Si—H bond. The silyl radicals in turn add to the unsaturated C—C bonds generating carbon-centered radicals that abstract hydrogen atoms from (Me₃Si)₃SiH, thus regenerating the silyl radicals.

We have also attempted the hydrosilylation of prop-2-en-1-ol **2** and 3-chloroprop-1-ene **1** in the absence of solvent^[18–21] and in the presence of air. We allowed the neat mixture (50 × 10^{−5} mol of substrate and 50 × 10^{−5} mol of (Me₃Si)₃SiH to stir for 48 h in an open vessel. After the reaction time elapsed, no hydrosilylation product is observed, and the substrate is recovered unaltered. From these results, water can be regarded as a good support medium for carrying out the radical chain transformation, as the solubility of oxygen in the neat substrate is compromised. In a recent report,^[22,23] we have managed to initiate the radical chain hydrosilylation reaction of C—C multiple bonded compounds in water with dioxygen, and found that this radical initiation is very sensitive to the dioxygen concentration.

As mentioned above, we have shown that in alkenyl-substituted 1,1-dichlorocyclopropane ring systems,^[12] the hydrosilylation of C—C double bonds under radical thermal initiation precedes the chlorine atom reduction in water; that is, the hydrosilylation of C—C double bonds is faster than the

chlorine atom removal by the (Me₃Si)₃Si radical and that the one-chlorine atom reduction occurs under forced reaction conditions. In the present study, we have found that substrate **1**, forms products **1a** and **1b** under thermal initiation. Formation of product **1a** and product **1b** can be accounted for from Scheme 3.^[12] Product **1a** arises from an ordinary hydrosilylation of the C—C double bond of **1**, while product **1b** is the result of a β-elimination of the chlorine atom from the intermediate radical species **I** (Scheme 3).

Hydrosilylation reactions of alkynes in water

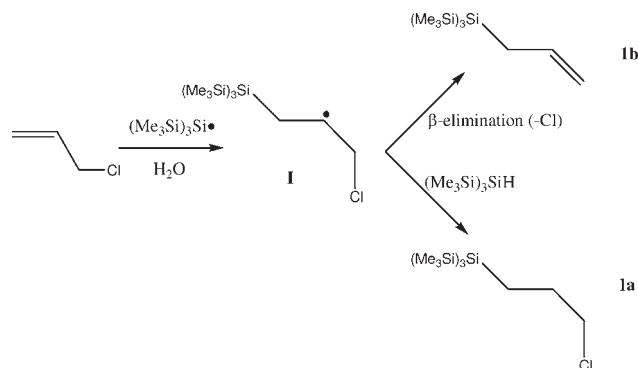
Recently, Zhou and coworkers^[21] reported that phenylacetylene is hydrosilylated in water in 1 h through air initiation to render the hydrosilylated product in 85% yield.

It is well-known that the hydrosilylation of alkynes^[13,24] in organic solvents takes place efficaciously under thermal initiation (AIBN), with the hydrosilylation products being obtained in high isolated yield, albeit in *E:Z* varying isomeric ratios. However, hydrosilylation of alkynes in water is very efficient and stereoselective under thermal initiation, as has been reported by us before.^[11,12,25,26] For example, the *Z:E* ratio for the hydrosilylated product derived from 1-cyclohexylacetylene changes from 45:55 in toluene (80 °C) to 74:26 in water (100 °C).^[11] Thus, in organic solvents the initiation with AIBN takes place efficaciously albeit with poor stereoselectivity, while in water, ACCN is preferably used as initiator, and the stereoselectivity is much higher.^[10,11] Recently, some of us have explored the hydrosilylation reactions of alkynes in water under dioxygen initiation, and have shown the high degree of stereoselectivity achieved under this milder initiation technique.^[12,22,23,25,26] For example, the *Z:E* ratio from hydrosilylation of 1-cyclohexylacetylene varies from 96:4 in toluene (25 °C, with Et₃B/air as initiator) to >99:1 in water (22 °C), under dioxygen initiation. More recently, these reactions are also performed in continuous-flow microreactors.^[27]

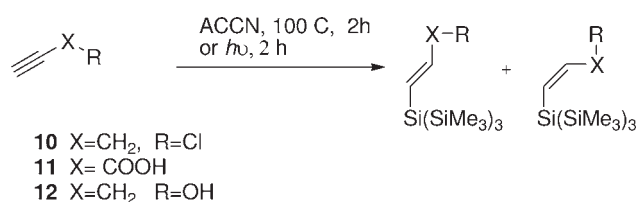
The hydrosilylation reaction of 3-chloroprop-3-yne (**10**), and propiolic acid (**11**) have been tested under photochemical initiation conditions, although in the latter case, 2-mercaptoethanol is added as the chain carrier.

The reactions proceed efficaciously affording the respective hydrosilylated alkenes in optimal reaction yields (90–95%, Scheme 4, Table 1, column 4, entries 10 and 11). These hydrosilylated alkenes are obtained with varying *Z:E* isomeric ratios.

The retention of the chlorine atom is observed in this hydrosilylated alkene product derived from substrate **10**.



Scheme 3. Proposed mechanism for formation of products **1a** and **1b** in water



Scheme 4. Hydrosilylation reactions of alkynes in water

Water-soluble hydrosilylated alkene products are rinsed with pentane (to discard silane excess), lyophilized, and column-chromatographed by reverse-phase silica with ethyl acetate-methanol as eluant. In some cases, the products are obtained sufficiently pure for spectral characterization (Supplementary Material).

For comparison, we report the hydrosilylation reaction of propiolic acid **11** with (Me₃Si)₃SiH in water initiated by light, where a high *Z:E* stereoselectivity ratio is obtained (Table 1, column 4, entry 11).^[11,12,25,26]

The hydrosilylation reaction of organic solvent-soluble 3-chloroprop-1-yne **10** and water-soluble prop-2-yn-1-ol **12** initiated by ACCN have been tested under the conditions described in Initiation by Thermal Decomposition of an Azo Compound Section, although in this latter case, 2-mercaptoethanol is added as the chain carrier. The reactions proceed efficaciously affording the respective hydrosilylated alkenes in optimal reaction yields (90%, respectively, Scheme 4, Table 1, column 3, entries 10, and 12). These alkenes are obtained with *Z:E* isomeric ratios varying from 50:50 (that from alkyne **10**) and 75:25 (that from alkyne **12**), determined by ¹H NMR spectroscopy.

For comparison, we report the hydrosilylation reaction of propiolic acid **11** with (Me₃Si)₃SiH in water initiated by ACCN (Table 1, column 3, entry 11), where a high *Z:E* stereoselection is obtained.^[11,12,25,26]

Unconjugated vinyl radicals are known to be sp² hybridized and to invert with a very low barrier (Eq. 1). The different stereoselectivity observed 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.



CONCLUSIONS

The scope of the hydrosilylation reaction of C—C multiple bonds in water with (Me₃Si)₃SiH 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 methods. Unlike the results known from photolysis of silanes in organic solvents,^[28] it is likely that, in water, the silyl radical production represents an important deactivating route of the singlet excited state of

silanes of the type (Me₃Si)₃SiH, since no silylene-derived products have been observed in detectable yields in the reactions initiated by light in water.^[28] We are currently exploring this silyl radical production in water with other starting silanes. Further work is also in progress in order to calculate the quantum yield of initiation of the radical-based photochemically-induced hydrosilylation reaction of C—C multiple bonds in water with (Me₃Si)₃SiH.

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REFERENCES

- [1] A. Langner, A. Panarello, S. Rivilio, O. Vassilyev, J. G. Khinast, Y. J. Chabal, *J. Am. Chem. Soc.* **2005**, *127*, 12798.
- [2] J. M. Schmeltzer, L. Porter, Jr., M. P. Stewart, J. M. Buriak, *Langmuir* **2002**, *18*, 2971.
- [3] M. P. Stewart, J. M. Buriak, *J. Am. Chem. Soc.* **2001**, *123*, 7821.
- [4] H. Yasuda, Y. Uenoyama, O. Nobutta, S. Kobayashi, I. Ryu, *Tetrahedron Lett.* **2008**, *49*, 367.
- [5] B. Marcinek, *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, **1992**.
- [6] B. Marcinek, *Silicon Chem.* **2002**, *1*, 155-165.
- [7] I. Ojima, Z. Li, J. Zu, *The Chemistry of Organic Silicon Compounds*, Vol. 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**.
- [8] C. Chatgililoglu, *Organosilanes in Radical Chemistry*, Wiley, Chichester, **2004**.
- [9] S. Amreim, A. Timmermann, A. Studer, *Org. Lett.* **2001**, *3*, 2357.
- [10] A. Postigo, C. Ferreri, M. L. Navacchia, C. Chatgililoglu, *Synlett.* **2005**, 2854.
- [11] A. Postigo, S. Kopsov, C. Ferreri, C. Chatgililoglu, *Org. Lett.* **2007**, *9*, 5159.
- [12] A. Postigo, S. Kopsov, S. Zlotzky, C. Ferreri, C. Chatgililoglu, *Organometallics* **2009**, *28*(11), 3282.
- [13] B. Kopping, C. Chatgililoglu, M. Zehnder, B. Giese, *J. Org. Chem.* **1992**, *57*, 3994.
- [14] M. Ballestri, C. Chatgililoglu, K. B. Clark, D. Griller, B. Giese, B. Kopping, *J. Org. Chem.* **1991**, *56*, 578.
- [15] B. M. Trost, Z. T. Ball, K. M. Laemhold, *J. Am. Chem. Soc.* **2005**, *127*, 10028.
- [16] A. Studer, H. Steen, *Chem. Eur. J.* **1999**, *5*(2), 759.
- [17] Indeed, upon silyl radical attack on the C—C double bond of **3**, the 1-amino-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)prop-2-yl radical would be formed. This latter radical, if S_Hi mechanism took place, would suffer bond cleavage and homolytic substitution at silicon to render, upon ulterior hydrogen abstraction, 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)butan-1-amine product, which was not found in the reaction mixture. It is interesting to note, that in ref. [16], the intermediate C-centered radical is proposed to abstract a hydroxyl hydrogen atom from the alcohol, rendering an O-centered radical which upon attack on the TMS group, renders the cyclic product, as it is analogously proposed in Scheme 2.
- [18] Y. Liu, S. Yamazaki, S. Yamabe, *J. Org. Chem.* **2005**, *70*, 556.
- [19] Y. Liu, S. Yamazaki, S. Yamabe, Y. Nakato, *J. Mater. Chem.* **2005**, *15*, 4906.
- [20] Y. Liu, S. Yamazaki, S. Izuhara, *J. Organomet. Chem.* **2006**, *691*, 5821.
- [21] J. Wang, Z. Zhu, W. Huang, M. Deng, X. Zhou, *J. Organomet. Chem.* **2008**, *693*, 2188.
- [22] A. Postigo, N. S. Nudelman, *J. Phys. Org. Chem.* DOI:10.1002/poc.1703.

- [23] J. Calandra, D. Russo, J. J. Tereñas, Thesis, Facultad de Ciencias Exactas y Naturales, Universidad de Belgrano, Buenos Aires, Argentina, **2009**.
- [24] K. Miura, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356.
- [25] A. Postigo, *Curr. Org. Chem.* **2009**, *13*(17), 1683.
- [26] A. Postigo, *Photochemical Generation of Silicon-centered Radicals and their Reactions. Chapter VI in "Progress in Photochemistry"*, Nova Science Publications, Hauppauge, New York, **2008**, pp. 193–226. ISBN 978-1-60456-568-3
- [27] A. Odedra, K. Geyer, T. Gustafsson, R. Gilmour, P. H. Seeberger, *Chem. Commun.* **2008**, 3025.
- [28] UV-Irradiation of $(\text{Me}_3\text{Si})_3\text{SiH}$ is known to generate silylenes rather than silyl radicals. We suggest that a minor photolytic path accounts for the formation of silyl radicals that initiate the radical chain hydrosilylation.