

Decatungstate Photocatalyzed Si-H/C-H Activation in Silyl Hydrides. Hydrosilylation of Electron-Poor Alkenes

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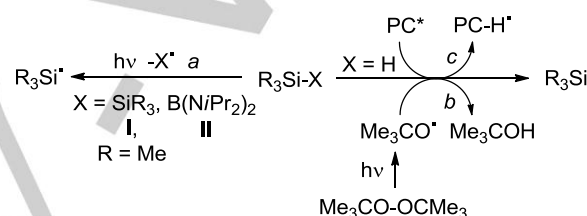
Abstract: Tetrabutylammonium decatungstate (TBADT) has been used for the photocatalyzed activation of the Si-H bond in trisubstituted silanes and applied for the hydrosilylation of electron-poor alkenes. The mechanism occurring depends on the silyl hydride used, as supported by Laser Flash Photolysis and EPR trapping experiments. A homolytic Si-H cleavage through a hydrogen atom transfer (HAT) from the silane to the excited catalyst operates with dimethylphenylsilane and methylphenylsilane, where the hydrosilylation yields were satisfactory. When using tertiary silanes having more labile Si-H bonds, such as triphenylsilane or tris(trimethylsilyl)silane, the reaction worked to some extent even under uncatalyzed conditions due to a radical chain reaction. Competition between C-H vs Si-H cleavage was observed, however, when using trialkylsilanes (e.g. triethylsilane). In favourable cases, the process was also efficient under flow conditions or when promoted by sunlight.

Introduction

The preparation of organosilanes via hydrosilylation is an important process that has found application in material science and medicine.^[1] Although various silylating agents can be used for this purpose,^[2,3] the direct activation of the Si-H bond in silyl hydrides (mainly trialkyl(aryl)silanes) is favored because it is atom-economic. This activation can take place either via transition-metal catalysis,^[4,5] by using Lewis acids^[6] or by homolysis of the Si-H bond to form silyl radicals.^[7,8] In the latter case, radical-chain hydrosilylation of alkenes using trialkylsilanes in the presence of a radical initiator (AIBN) has been sparsely reported.^[7] Addition of silyl radicals onto electron-rich alkenes, however, is hindered by the fact that hydrogen-atom donation from the starting silane to the adduct-radical formed is relatively slow, so that telomerization of the olefin compete. A polar-reverse catalysis making use of thiols has been used to overcome this problem, albeit in some cases the thiol had to be added slowly with a syringe pump to avoid competitive thiol addition onto the alkene.^[9,10] As for addition of R_3Si^\bullet onto electron-poor olefins,^[11,12] the hydrosilylation is not common and mostly involves $(TMS)_3Si^\bullet$,^[11,13-15] where it occurs with a significant absolute rate constant ($k_{add} > 10^7 \text{ M}^{-1} \text{ s}^{-1}$).^[13]

Photochemistry offers an appealing and less exploited approach for the generation of silyl radicals (Scheme 1).^[16] The

photolysis of a Si-Si bond (e.g. in $Me_3Si-SiMe_3$, **I**) is feasible but found no application in synthesis as yet.^[16,17] Only recently the photohomolytic cleavage of the Si-B bond in bis(diisopropyl-amino)organosilylboranes (**II**) was applied for the hydrosilylation of both electron-donating and electron-withdrawing substituted olefins (path a).^[18] An obvious alternative is the hydrogen atom transfer from a Si-H bond to a photogenerated *tert*-butoxyl radical (path b)^[19] or to an excited photocatalyst (PC, Scheme 1, path c), usually an aromatic ketone (e.g. benzophenone, xanthone).^[20]



This work PC = $(n-Bu_4N)_4[W_{10}O_{32}]$

Scheme 1. Photochemical generation of silyl radicals. PC = Photocatalyst.

In the last years, tetrabutylammonium decatungstate (TBADT, $(n-Bu_4N)_4[W_{10}O_{32}]$)^[21] has been conveniently adopted as a photocatalyst^[22] for the regioselective activation of C-H bonds in organic compounds for the formation of valuable C-C,^[23] C-N^[24] and C-F bonds.^[25] In the present work we addressed the TBADT-photocatalyzed activation of the Si-H bond in silanes for the hydrosilylation of electron-poor olefins.^[26]

Results and Discussion

Preparative experiments. The TBADT photocatalyzed reaction between dimethylphenylsilane (**1a**) and dimethyl maleate (**2a**) caused the hoped for hydrosilylation (Table 1). When an acetonitrile solution containing TBADT ($2 \times 10^{-3} \text{ M}$; 2 mol%) and an equimolar amount (0.1 M) of **1a** and **2a** was exposed to UV light ($10 \times 15 \text{ W}$ low pressure phosphor-coated lamps centered at 310 nm) for 24 h, silane **3** was formed in 65% yield with a partial consumption of the olefin (entry 1). The yield and the efficiency of the process were increased by increasing the amount of **1a** up to 0.2 M (entries 2-3). The reaction conditions as from entry 3 were chosen for testing different irradiation modes. Using lamps emitting at a longer wavelength (366 nm) gave a poor result (46% yield of **3**, entry 4), whereas the reaction proceeded satisfactorily under either simulated or direct solar light (75% and 66% yield, respectively, entries 5-6). Both light and the photocatalyst were required, as demonstrated by blank experiments (entries 7-8).

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Table 1. TBADT photocatalyzed reaction of dimethylphenylsilane (**1a**) with dimethyl maleate (**2a**).^[a]

Entry	1a , M	2a , M	2a Consumption, %	3 Yield, % ^[b]
1	0.1	0.1	69	65
2	0.15	0.1	80	66
3	0.2	0.1	100	73
4 ^[c]	0.2	0.1	100	46
5 ^[d,e]	0.2	0.1	100	75
6 ^[e,f]	0.2	0.1	100	66
7 ^[g]	0.2	0.1	34	7
8 ^[h]	0.2	0.1	3	0

[a] The reaction mixture was irradiated in a multi-lamp apparatus fitted with 10x15W low pressure phosphor-coated lamps (irradiation centered at 310 nm). [b] GC yields based on **2a** consumption. [c] Lamps centered at 366 nm were used. [d] Irradiation by a SolarBox equipped with a 1.5 kW Xe lamp (500 W m⁻²). [e] Reaction carried out in a Pyrex glass vessel (20 mL capacity, see ref 27). [f] Irradiation by direct sunlight (5 days; 8h per day, see ref. 27). [g] No TBADT added. [h] Reaction carried out in the absence of light.

The reaction was then explored by reacting **1a** and further phenyl silanes **1b-c** in the presence of representative electron-poor olefins **2a-f** under the conditions reported in Table 1, entry 3 (see Table 2). The hydrosilylation reactions of phenyl vinyl sulfone (**2b**), methyl methacrylate (**2c**) and acrylonitrile (**2d**) by **1a** were successful (up to 85% yield, compounds **4-6**; entries 2-4), while a modest yield and stereoselectivity (36%, 4:1 *endo/exo* ratio) were obtained in the reaction with methylene norbornanone (**2e**; entry 5). Likewise, using methyldiphenylsilane **1b** satisfactory silylation yields were obtained from unsaturated esters and nitriles to form compounds **8-11** (entries 6-9). The yield was lower when using an α,β -unsaturated ketone (e.g. cyclopentenone **2f**). Succinate **8** was also formed to some extent (28%) even in the absence of TBADT. The reaction proceeded also with bulky triphenylsilane **1c**, although with somewhat lower yields and compounds **12-14** were obtained. The first one, resulting from the reaction with **2a**, was formed in a modest yield (45%) even under uncatalyzed conditions (entry 10). By contrast, the hydrosilylation of dimethyl maleate **2a** with tris(trimethylsilyl)silane (**1d**, 0.15 M due to solubility problems, entry 13), proceeded well even in the absence of the catalyst.

With trialkylsilanes, the reaction was more complex, with C-H activation competing to some degree.^[23] Thus, the reaction between triethylsilane (**1e**) and acrylonitrile (**2d**) yielded a mixture of three isomeric adducts (**16a-c**), arising from the functionalization at the Si-H, methylene and methyl groups, respectively, in a 3:1:1 ratio with an overall yield of 50% (Scheme 2a). Replacing benzophenone (0.1 M) for TBADT led

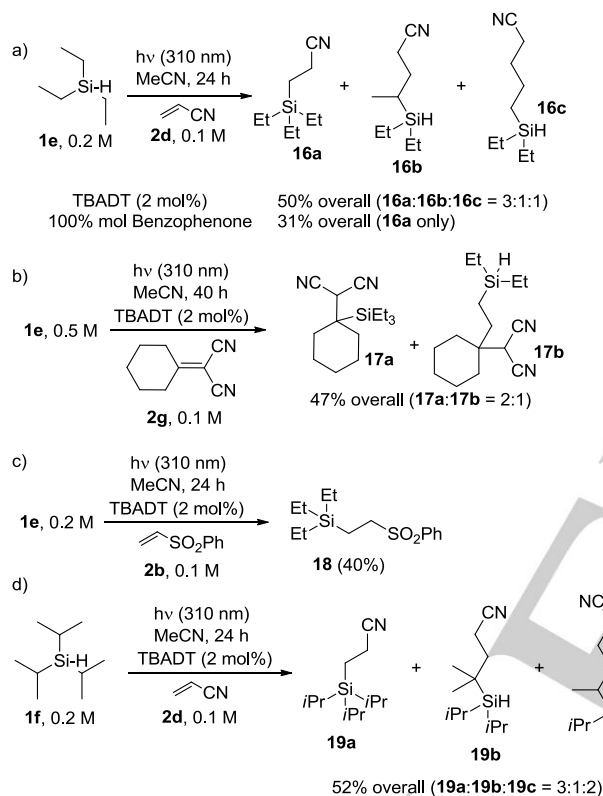
to the formation of 3-triethylsilylpropanenitrile (**16a**) only in a low yield (31%). The reaction between **1e** (in this case used 0.5 M to allow complete consumption of the olefin) and sterically hindered cyclohexylidene malononitrile **2g** gave a mixture of two isomeric adducts in a 2:1 ratio resulting from the functionalization at the Si-H (**17a**) and at the methyl group (**17b**, 47% overall yield; Scheme 2b).

Table 2. TBADT photocatalyzed hydrosilylation of electron-poor olefins.^[a]

Entry	Silane 1	Olefin 2	Product, yield ^[b]
1	1a R ¹ = R ² = Me R ³ = Ph	2a	3 , 70
2	1a	2b	4 , 80
3	1a	2c	5 , 85
4	1a	2d	6 , 66
5	1a	2e	7 , 36 ^[c]
6	1b R ¹ = Me R ² = R ³ = Ph	2a	8 , 90 28 ^[d]
7	1b	2c	9 , 76
8	1b	2d	10 , 65
9	1b	2f	11 , 40
10	1c R ¹ = R ² = R ³ = Ph	2a	12 , 63 45 ^[d]
11	1c	2d	13 , 44
12	1c	2f	14 , 47
13	1d ^[e] R ¹ = R ² = R ³ = SiMe ₃	2a	15 , 80 82 ^[d]

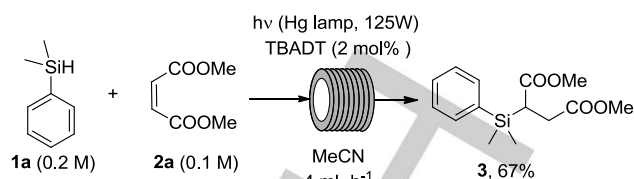
[a] Reaction conditions: A solution of the silane (0.2 M), the electrophilic alkene (0.1 M) and TBADT (2x10⁻³ M) in CH₃CN was poured in a quartz tube and irradiated at 310 nm (in a multi-lamp apparatus fitted with 10 phosphor-coated lamps, 15W each) for 24 h. [b] Isolated yields after silica gel chromatography (cyclohexane/ethyl acetate as the eluants). [c] *endo:exo* ratio = 4:1 (see SI for details). [d] Reaction carried out in the absence of TBADT. [e] 0.15 M **1d**.

Si-H functionalization was the only process occurring in the photocatalyzed addition of **1e** onto **2b** leading to silane **18** (40% yield; Scheme 2c). Again three products were obtained from trisopropylsilane **1f** and acrylonitrile **2d**, *viz.* adducts **19a-c** (52% overall yield) resulting from the functionalization at the Si-H, methine and methyl groups in a 3:1:2 ratio, respectively. The extension of the reaction to different silanes was next pursued. Mono- and disubstituted silanes (e.g. *n*-butyl silane **1g**, phenylsilane **1h** and diphenylsilane **1i**) were tested in the reaction with **2a** but no olefin functionalization occurred ($\leq 10\%$ olefin conversion).



Scheme 2. Photocatalyzed reaction of trialkylsilanes with electron-poor olefins.

With the aim of shortening the reaction time, we turned to flow conditions by wrapping coils of a tubing (made of UV-transparent polytetrafluoroethylene, PTFE; outer diameter: 1.6 mm, inner diameter: 1.3 mm) around a water-cooled immersion well apparatus (see Figure S3, Supporting Information).^[23f] The designed photochemical reactor had a 12 mL capacity and made use of a medium pressure (125 W) Hg-vapors lamp equipped with a flow-through back-pressure unit.^[23f] A MeCN solution containing **1a**, **2a** and TBADT was charged into a syringe and circulated by means of a syringe pump with a flow rate of 4 mL h⁻¹. To our delight, this experimental setup allowed a complete conversion of the reagents with a significant shortening of the irradiation time (from 24 to 3 h, Scheme 3) while maintaining the yield found under batch conditions.



Scheme 3. Photocatalytic addition of silane **1a** onto maleate **2a** under flow conditions.

Mechanistic studies. More insight on the mechanism involved was sought for with selected silanes (**1a-1c**, **1e**, **1i**). Thus, laser flash photolysis (LFP) experiments were carried out (Figure 1). Flashing ($\lambda = 355\text{ nm}$) the decaying solution allowed to measure the decay of the TBADT reactive excited state at $\lambda = 780\text{ nm}$. At the same wavelength, a long-lived signal, attributable to $[\text{HW}_{10}\text{O}_{32}]^{4-}$, became more and more intense (see the arrows in Figure 1) in the presence of increasing amounts of the silanes. The measured bimolecular quenching constants (k_Q) revealed that reaction of excited TBADT with **1a** ($k_Q = 7.0 \times 10^7\text{ M}^{-1}\text{ s}^{-1}$, Figure 1a) was slightly faster than those with silanes **1b**, **1e**, **1i** (k_Q in the $2.8\text{--}3.8 \times 10^7\text{ M}^{-1}\text{ s}^{-1}$ range, Figures 1b, 1d, 1e). On the contrary, addition of triphenylsilane **1c** caused only a minimal change to the signal registered in neat acetonitrile, independently from the concentration of the silane (Figure 1c).

Steady state EPR experiments were also carried out in the presence of α -phenyl *N-tert*-butyl nitron (PBN) in the role of spin trap.^[29] Thus, irradiation of TBADT in neat MeCN in the presence of 0.05 M PBN gave rise to a signal consisting in a triplet of doublets ($a_N = 14.5\text{ G}$; $a_H = 2.95\text{ G}$) that could be attributed to the trapping of the cyanomethyl ($\cdot\text{CH}_2\text{CN}$) radical, in agreement with previous reports (see Figure S2 and Table S2 for details).^[26,30] When the same experiment was carried out in the presence of 0.1 M **1a**, a triplet of doublets with different coupling constants was observed. This was recognized as due to the trapping of the $\text{PhMe}_2\text{Si}\cdot$ radical, with $a_N = 14.7\text{ G}$; $a_H = 5.73\text{ G}$ (Figure 2a), in fair agreement with previous reports.^[26,31] In addition, a low amount of C-centered radicals ($< 10\%$) was likewise detected in the spectrum. Similarly, experiments on **1b** evidenced the trapping of the $\text{Ph}_2\text{MeSi}\cdot$ radical ($a_N = 14.6\text{ G}$; $a_H = 6.20\text{ G}$) along with a minor contribution due to C-centered radicals (Figure 2b). A weak signal was obtained from the $\text{Ph}_3\text{Si}\cdot$ radical ($a_N = 14.6\text{ G}$; $a_H = 6.34\text{ G}$, Figure 2c). When using **1e** (0.1 M), a very similar signal as that observed in the case of **1a** was found ($a_N = 14.7\text{ G}$; $a_H = 5.36\text{ G}$), likewise attributable to the trapping of a silyl radical (Figure 2d). This was accompanied by a minor signal (15% *ca.* on the basis of the double integration of the EPR signal), with the same multiplicity, but with different coupling constants, typical of a C-radical ($a_N = 14.6\text{ G}$; $a_H = 3.00\text{ G}$). Trapping of the silyl radical $\text{Ph}_2\text{SiH}\cdot$ ($a_N = 14.6\text{ G}$; $a_H = 7.23\text{ G}$) arising from aromatic secondary silane **1i** was quite inefficient and EPR experiments showed a strong contribution from C-radicals (more than 30%; Figure 2e).

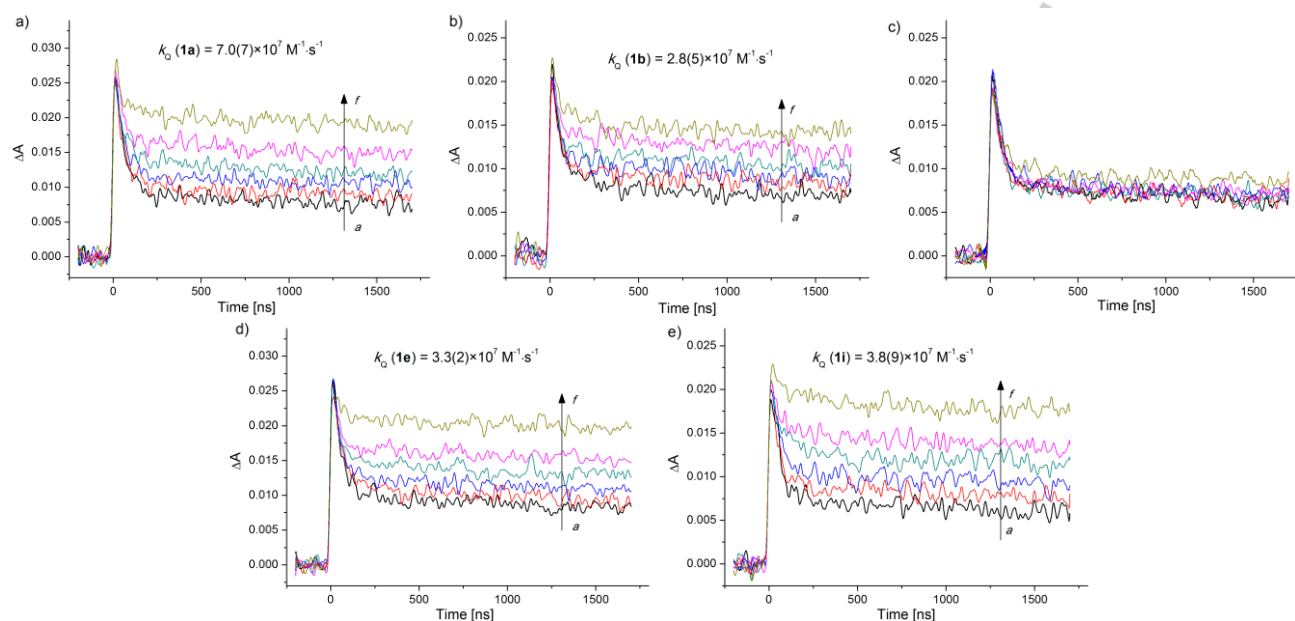


Figure 1. Transient absorption at $\lambda = 780$ nm observed upon flashing ($\lambda = 355$ nm) a 2×10^{-4} M TBADT solution in MeCN (a, bold black line) and in the presence of increasing amounts (from b to f, see Table S1 for details) of: a) **1a**, b) **1b**, c) **1c**, d) **1e** and e) **1i**.

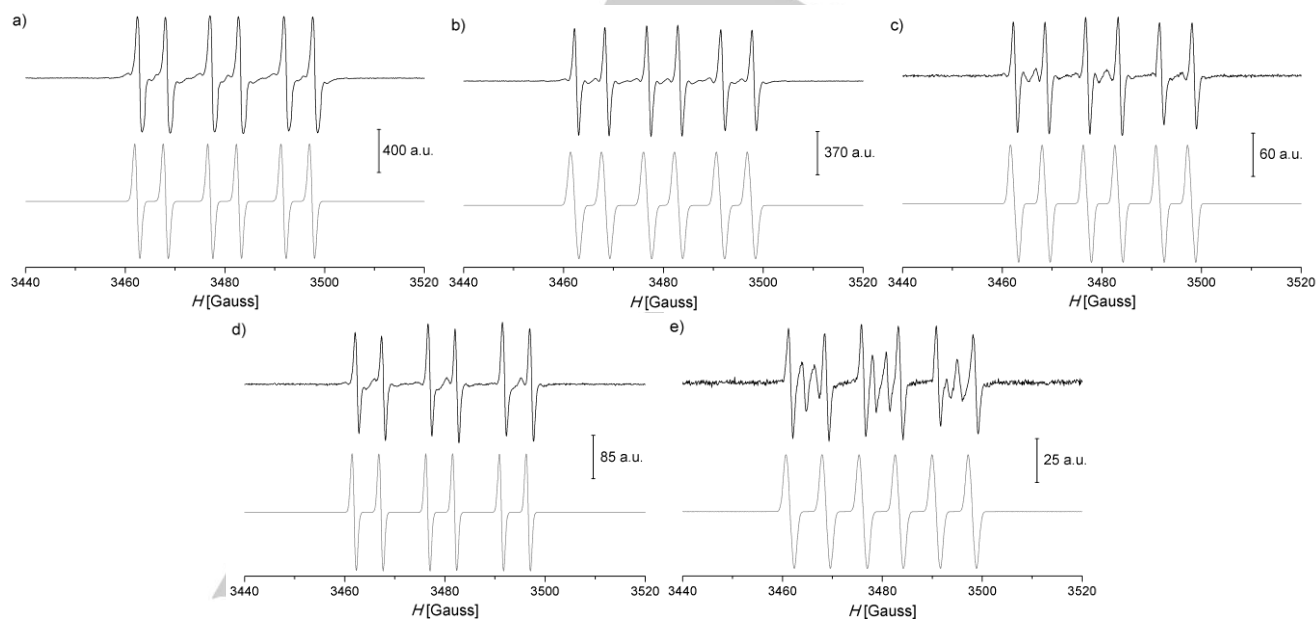


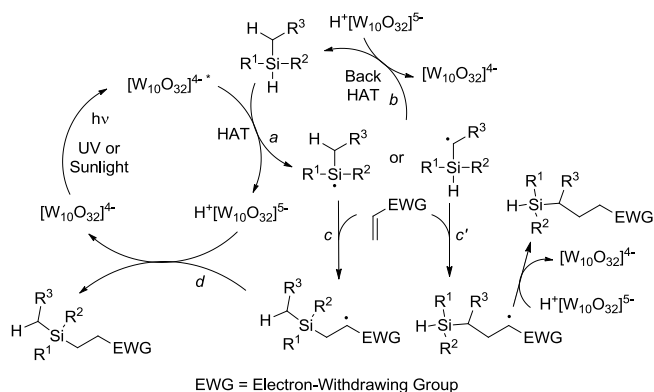
Figure 2. Experimental (up) and simulated (down; only the most important contribution shown) EPR spin trapping spectra obtained irradiating ($\lambda > 300$ nm) a MeCN solution of TBADT (2×10^{-3} M) containing: a) **1a** (0.1 M), b) **1b** (0.1 M), c) **1c** (0.1 M), d) **1e** (0.1 M) and e) **1i** (0.1 M) in the presence of α -phenyl *N*-*tert*-butyl nitrene (PBN, 0.05 M). a.u. = arbitrary units.

Discussion. The present work demonstrates that electronically excited decatungstate is able to activate the Si-H bond in trisubstituted silanes for the hydrosilylation of olefins. The behavior of excited TBADT resembles that of an alkoxy radical (e.g. *tert*-butoxy,^[20a] phthalimide-*N*-oxyl (PINO)^[32]) and

that of excited ketones (e.g. benzophenone^[20b]) in the reaction with R_3Si-H .

Three mechanisms can be distinguished as apparent from the data summarized in Table 3. In the case of substituted phenylsilanes **1a-1b**, and **1e-1f**, excitation of the photocatalyst

leads to homolytical Si-H bond cleavage (Scheme 4, path a). The silyl radical formed then attacks the β -position of the electrophilic alkene forming a radical adduct (path c) that receives back the hydrogen atom from the reduced photocatalyst, finally leading to the desired silylated product (path d).



Scheme 4. Proposed reaction mechanism for silanes **1a-1b**, **1e-1f**.

The occurrence of a Hydrogen Atom Transfer (HAT) mechanism is supported by LFP experiments, where the detection of the persistent absorption at 780 nm due to the $[HW_{10}O_{32}]^{4-}$ species is in accordance with previous reports for other hydrogen donors.^[33] The quenching rate constant found for silane **1a** ($k_Q = 7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) is fairly in agreement with that measured by the group of Prof. Lalevee ($k_Q = 4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, Table 3).^[26] Excited TBADT is an efficient catalyst for the cleavage of the Si-H bond if compared to *t*-BuO \cdot or triplet benzophenone, where the rate constant for the formation of a silyl radical from Et₃SiH is lower ($k_Q \leq 10^7 \text{ M}^{-1}\text{s}^{-1}$).^[20b] The alternative possibility of single electron oxidation followed by deprotonation can be safely excluded due to the high oxidation potentials of the silanes used.^[34] EPR trapping experiments with nitron confirmed the role of both Si- and C-centered radicals, the latter in a low yield (< 15% with respect to the amount of Si-centered radicals detected, Table 3). Consider that a part of the signal is due to trapping of the cyanomethyl (CH_2CN) radical from the solvent.

The overall course of the reaction depended on the competition between back hydrogen atom transfer (Scheme 4, path b) and addition onto the electron-poor olefins (paths c and c'). As for the last process, the rate constant for addition of an alkyl radical onto an electron-poor olefin (k_{add}) is in the $1\text{-}5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ range,^[35] markedly lower than that measured for the triethylsilyl radical (with acrylonitrile: $k_{\text{add}} = 1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; with methyl acrylate: $k_{\text{add}} = 2.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, Table 3).^[20b] Thus, in the first mechanism only silyl radicals were trapped in the reaction of **1a** (and **1b**), to the exclusion of C-centered radicals, despite the fact that both are formed, as revealed by EPR and expected on the basis of the similar k_Q values measured for dimethylphenylsilane ($k_Q = 7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) and diphenylmethylsilane ($k_Q = ca.$

$3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) on one hand, and that determined for a methylene group in a cycloalkane ($k_Q = 4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ for cyclohexane).^[23a]

On the other hand, both Si- and C-centered radicals were trapped when trialkylsilanes **1e**, **1f** were used, although the fraction of products from Si-centered radicals trapped by alkenes was lower than that from trapping by PBN. In this second mechanism, the proportion depended on the structure of both silane and alkene. As for the former, more labile methylene and methine C-H groups in the starting silane (compare e.g. the BDE of the C₂-H bond in structurally related 2-methylbutane, reported to be in the 91.6 to 96.5 kcal mol⁻¹ range)^[36] increased the amount of C-centered radicals, in particular in silane **1f**, where the portion of carbon radical adducts is ca. 50%.

As for the olefin role, considering the reaction of **1e** with olefins **2d**, **2g** and **2b**, the strongly electrophilic vinyl sulfone **2b**^[37] traps exclusively the Si-centered radicals, while the lower reactivity of **2d** (a less electrophilic olefin) and **2g** (due to steric hindrance at the β -position) leaves room for back hydrogen-atom donation, resulting in the formation of ca. 30-35% of C-radical trapping products. Benzophenone is a less efficient H-abstracting species than TBADT and only silane **16a** was formed, though in a low yield (31%).

The third mechanism refers to the case of tertiary silanes having more labile Si-H bonds, as in the case of **1c** and **1d**. Table 3 collects the Bond Dissociation Energies (BDE) of the Si-H bond in the silanes tested. Calculated values were preferred, since the literature experimental values are not sufficiently precise for a realistic comparison.^[36]

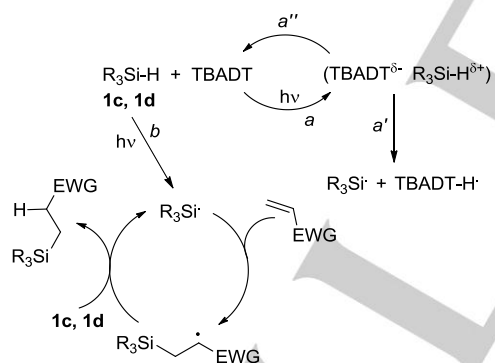
Table 3. Some important data related to the TBADT-photocatalyzed hydrosilylation of electron-poor olefins.

H donor	$k_Q (\text{M}^{-1}\text{s}^{-1})$ ^[e]	k_{add} ^[b]	BDE Si-H (kcal mol ⁻¹)	EPR signal ^[c]
PhMe ₂ SiH (1a)	7×10^7 ^[d] (4×10^7) ^[e]		91.3 ^[f]	Si 400 C 10
Ph ₂ MeSiH (1b)	2.8×10^7 ^[d]		90 ^[f]	Si 370 C 20
Ph ₃ SiH (1c)	^[g]		88.6 ^[f]	Si 60 C 7
(Me ₃ Si) ₃ SiH (1d)	4×10^7 ^[e]	$5\text{-}6 \times 10^7$ ^[h,i] 2.2×10^7 ^[i,j]	82.3 ^[f]	[k]
Et ₃ SiH (1e)	3.3×10^7 ^[d]	1.1×10^9 ^[h,i] 2.4×10^9 ^[i,j]	92.8 ^[f]	Si 85 C 7
Me ₃ SiH			93.2 ^[f]	
Ph ₂ SiH ₂ (1i)	3.8×10^7 ^[d] (6×10^7) ^[e]			Si 25 C 8
MeCN	8.4×10^5 ^[l]		96 ^[f] (C-H)	C 4

[a] Bimolecular quenching constants (k_Q). [b] Rate constant (k_{add}) for the addition of the silyl radical to electron-poor olefins. [c] Intensity of the signal due to the trapping of photogenerated Si-/C-based radicals by PBN (in arbitrary units). [d] This work. [e] From ref. 26. [f] From ref. 38. [g] Too low to be measured, see text. [h] With acrylonitrile. [i] From ref. 12. [j] With methyl acrylate. [k] Not measured. [l] Value in s⁻¹, From ref. 23i.

It is widely accepted that the substitution of a hydrogen atom for an alkyl group in silanes slightly decreases the BDE of the Si-H bond,^[38,39] whereas there is a poor stabilization of silicon-centered radicals by neighboring phenyl groups, contrary to what observed with related carbon-centered benzyl radicals.^[38,40] Actually, compound **1e** (a trialkylsilane) has the highest BDE of the series (92.8 kcal mol⁻¹). The BDE slightly decreases, however, when substituting a methyl group for a phenyl group (compare the values of **1a** and Me₃Si-H in Table 3).

The LFP pattern observed for **1c** (Figure 1c) is completely different from that of the other silanes and resembles that observed when using toluene as the hydrogen donor.^[23d] Formation of the Ph₃Si[•] radical is inefficient as apparent from the EPR experiments, (Figure 2c, where carbon-centered radicals were present and arose exclusively from the solvent (hydrogen abstraction from H-CH₂CN, (96 kcal mol⁻¹)^[36] by Ph₃Si[•] radical is thermodynamically unfavorable). The high amount of hydrosilylation product formed under uncatalyzed conditions (Table 2, entry 10) supports the occurrence of a chain reaction initiated by the direct photocleavage of the Si-H bond in **1c**^[16a] (see the UV spectrum in Figure S1). The same applies to silane **1d** that has a very labile Si-H bond (BDE = 82.3 kcal mol⁻¹, Table 3) where the role of the photocatalyst is marginal (Table 2). Thus, in this case (Scheme 5) photocatalysis leads to a polar exciplex (path a) from which deactivation (path a'') predominates over Si-H bond cleavage (path a'), differently from the mechanisms listed above (Scheme 4). The amount of the Ph₃Si[•] formed, however, is sufficient to initiate a chain reaction where a strong C-H bond is formed at the expense of a labile Si-H bond, and is initiated also by direct absorption (path b, Figure S1).^[16a]



Scheme 5. Proposed reaction mechanism for silanes **1c**, **1d**.

Finally, no hydrosilylation took place with mono- and di-substituted silanes (compounds **1g-i**). Previous LFP literature reports^[26] and our own measurements (Figure 1e) showed that quenching rate constants of excited decatungstate by **1a** and **1i** are similar to the other cases and this leads to the expectation that hydrogen abstraction from disubstituted silanes occurs with the same efficiency as in trisubstituted analogs. The fact that trapping of silyl radicals is inefficient both by PBN (Figure 2e) and by alkenes supports that efficient back hydrogen-atom donation (Scheme 4, path b) or another decomposition of these

short-lived radicals operates.^[44] The same holds for the case of primary silanes **1g**, **1h**.

From the practical point of view, the photocatalyzed hydrosilylation of olefins is efficient when the silane bears at least one phenyl group, as in the case of **1a-c**, or a very reactive olefin is used (e.g. **2b**). Furthermore, in all of the reactions tested, no competitive silyl radical addition onto the carbonyl or carboxylic moieties (when present) has been observed.^[42]

Conclusions

The Si-H activation in trisubstituted silanes takes place under mild conditions and does not require any toxic (e.g. tin hydrides), expensive or potentially explosive (e.g. peroxides) initiators to promote the process and can be easily performed under continuous flow conditions. Moreover, the capability of the photocatalyst to absorb in the UV-A region^[27] allows the use of sunlight to carry out the desired hydrosilylation, with no need to waste energy for the lamps operation, thus making the process green.^[43] Aromatic tertiary silanes give clean hydrosilylation reactions with satisfactory to good yields, while less reactive aliphatic derivatives give mainly mixtures where the products distribution is dependent on the olefin structure.

Experimental Section

General procedure for the photocatalyzed hydrosilylation of electron-poor olefins. An acetonitrile solution (30 mL) of the silane (**1**, 0.15-0.2 M; 4.5-6 mmol) and the olefin (**2**, 0.1 M; 3 mmol) in the presence of 200 mg of TBADT (2×10^{-3} M) was poured in two quartz tubes and purged for 5 minutes with nitrogen, septum capped and irradiated for 24 h with ten 15W phosphor-coated lamps (emission centered at 310 nm). The solvent was removed in vacuo from the photolyzed solutions and the products isolated by purification of the residue by column chromatography (cyclohexane/ethyl acetate as eluents).

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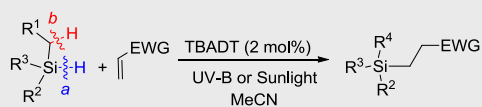
Keywords: Decatungstate salts • Hydrosilylation • Photocatalysis • Silanes • Silyl radicals

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Path a: Homolytic cleavage exclusive with PhMe₂SiH and Ph₂MeSiH

Path b: Competitive C-H cleavage with Et₃SiH and iPr₃SiH

Radical chain reaction with Ph₃SiH and (Me₃Si)₃SiH

Hisham Qrareya, Daniele Dondi, Davide Ravelli, * and Maurizio Fagnoni*

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Decatungstate Photocatalyzed Si-H/C-H Activation in Silyl Hydrides. Hydrosilylation of Electron-Poor Alkenes

Photocatalytic Si-H cleavage: Tetrabutylammonium decatungstate (TBADT) has been used for the photocatalyzed activation of the Si-H bond in trisubstituted silanes and applied for the hydrosilylation of electron-poor alkenes. The mechanism occurring is dependent on the silane used and competition between C-H vs Si-H cleavage was likewise observed.