Air-initiated hydrosilylation of unactivated alkynes and alkenes and dehalogenation of halohydrocarbons by tris(trimethylsilyl)silane under solvent-free conditions

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ABSTRACT

A highly efficient air-initiated hydrosilylation of unactivated alkynes and alkenes and dehalogenation of halohydrocarbons with tris(trimethylsilyl)silane ((TMS)$_3$SiH) as a reducing agent has been established under solvent-free conditions. These observations demonstrate that the potential and versatility of air to function as a competent initiator for Si–H bond activations. It can rival organic initiators and metal catalysts in its efficiency and is a superior initiating system from economic, environmentally sound and practical perspectives.

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1. Introduction

The addition of Si–H bond to alkynes is one of the most important reactions for the preparation of the corresponding vinyl silanes, which are versatile building blocks in organic synthesis [1]. On the other hand, from the various procedures and reagents that have been developed for reductive dehalogenation, the silanes also represent an important family due to their low toxicity, fewer by-products and compatibility with a wide range of solvents [2]. Nevertheless, silanes are known to be the poor reducing agents, due to their low ability to donate hydrogen atoms or hydrides [3]. In general, the Si–H bond needs to be activated by organometallic complexes [4], radical initiators [5] or irradiation [6] in these processes. Although quite efficient, organometallic complexes are usually expensive and/or water-sensitive while organic radical initiators generally require the elevated temperature [7]. Furthermore, in the two cases, especially for metal-based catalytic system, a use of organic solvents is generally necessary. The concerns of environment-pollution due to the extensive use of volatile organic solvents and metal-containing reagents calls for more convenient and cleaner methods to activate the Si–H bonds under mild conditions.

A simple and cheap approach to making the silyl radical reaction process environmentally clean/green would be carried out in the absence of any solvent, using a clean initiator instead of the organic initiators, preferably using ubiquitously molecular oxygen for favorable process economics. Although silanes have been known to undergo oxidation reactions with O$_2$ via an radical mechanism at least since 1992 [8], to our surprise, relatively little effort has been devoted to the development of the reactions as an effective initiating system for silyl radical reactions. Only recently, a few successful examples of air-induced hydrosilylation of activated alkenes and alkynes were reported [9]. Compared with traditional methods for activation of Si–H bonds, these reactions are cleaner, simpler, and more economic without the need of organic radical initiators or metal complex catalysts. However, attempts to extend the strategy to simple alkenes and alkynes were unsuccessful [9a]. Very recently, during our research into initiating silyl radical reactions by lanthanide metals [10], we accidentally observed that a small amount of air (dioxygen) could induce the addition of (TMS)$_3$SiH to phenylacetylene to give the corresponding *anti*-Markovnikov hydrosilylation product in a good yield. To probe the scope of air-induced silyl radical reactions and to understand factors controlling required selectivity and mildening reaction conditions, in this paper we present an extension of air-initiated hydrosilylation to unactivated alkynes and alkenes. Furthermore,

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we found that air is also an efficient initiator for radical dehalogenation of halohydrocarbons using $(TMS)_3SiH$.

2. Results and discussion

Phenylacetylene was used as model substrate to optimize the reaction conditions. As shown in Table 1, under pure argon atmosphere (using standard Schlenk technique), the reaction between phenylacetylene and $(TMS)_3SiH$ in THF did not take place even at 60 °C for 48 h (Table 1, entry 1). When 2.0 mL air was introduced into the vial, the hydrosilylation product was obtained in 87% yield at ambient temperature for 2 h (Table 1, entry 2). However, when the reaction was carried out under air atmosphere (Table 1, entries 3 and 4), the yield of the addition product was low due to the predominant formation of $(Me_3SiO)_2SiHSiMe_3$ [8,11], indicating that the ratio of reagents, particularly air/silane, is important for the reaction. In addition, we examined the effect of solvents, H_2O was found to be an effective solvent for this transformation despite not being substrates-soluble (Table 1, entry 6) [12]. But the reaction proceeded more quickly under solvent-free conditions and afforded Z-isomer in the highest yield (Table 1, entry 7). Significantly, the selectivity and yield obtained in the present system are comparable to those observed in the Et_3B/O_2 initiating system, and no solvent is needed [13]. To the best of our knowledge, only a few reports are available about solvent-free silyl radical reactions in the literature [9]. Among various silanes examined, $(EtO)_3SiH$, Et_3SiH and Ph_2MeSiH are inefficient substrates even with prolonged heating (Table 1, entries 13–15).

To explore the generality of this reaction, we then tested the hydrosilylation of various alkynes under optimum reaction conditions. The results are summarized in Table 2. All reactions gave anti-Markovnikov addition products in moderate to excellent yields. The reactivity of alkynes is controlled by the nature of the substituents. Aromatic acetylenes undergo most readily the hydrosilylation to give the Z-isomers in high yields and with excellent regio- and stereoselectivity, whereas straight chain alkyl groups seem to negatively effect the percentage distribution of isomers (Table 2, entries 9 and 10). This is consist with the previously

observation [13]. The presence of cyclohexenyl did not interfere with the outcome of the reaction of alkyne (Table 2, entry 5), although the sole C–C double bond has been found to be reactive to $(TMS)_3SiH$ under the similar conditions (vide infra). However, the aliphatic alkynes, bearing ether groups, reacted sluggishly and gave the desired products in moderate to good yields (Table 2, entries 6 and 7). The selective hydrosilylation of propargylic alcohols in a general sense was a challenging problem due to the competitive formation of the endo-dig cyclization products [14]. Significantly, in the present case $C_6H_5CH(OH)C\equiv CH$ reacted with $(TMS)_3SiH$ to give the highly selective hydrosilylation product albeit moderate yield (Table 2, entry 8). Furthermore, treatment of 1,6-heptadiyne with 1 equiv. of $(TMS)_3SiH$ also gave the selective mono-hydrosilylation product in respectable yield (Table 2, entry 11).

These successful results encouraged us to extend the method to the hydrosilylation of unactivated alkenes. Table 3 summarizes the results. Similar to those described for the hydrosilylation of alkynes, the reaction of $(TMS)_3SiH$ with unactivated alkenes was also markedly promoted by a catalytic amount of air under mild conditions to give the corresponding anti-Markovnikov addition products in moderate to good yields (Table 3). The electron-withdrawing or electron-donating substituent in benzene ring seems to have little effect in the yields (Table 3, entries 1, 5 and 6). It is worth mentioning that both the use of a slight excess of $(TMS)_3SiH$ (1.1 equiv.) and the control of the catalytic amount of air are the keys to the success of these hydrosilylation reactions to prevent the oligomerization of alkynes/alkenes and the formation of siloxane.

It is well-known that tris(trimethylsily1)silane can function as a free radical reducing agent for organic halides. However, the reactions generally need to be initiated by UV photolysis or by the thermal decomposition of organic initiators in the presence of solvents [15]. To further explore the scope and limitations of the air-induced silyl radical reactions, we then turned our attention to the reaction of $(TMS)_3SiH$ with a variety of organic halides. Several solvents and conditions were tried and we have found that optimum results were obtained by using 1–2 mol% of O_2 based on halides. As

Table 1
Hydrosilylation of phenylacetylene under different conditions[a]
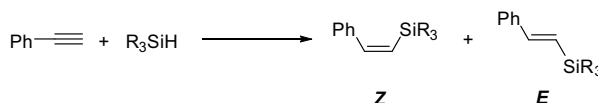
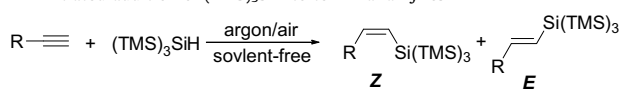| Entry	Silane	Additive	Solvent	T (°C)	Time (h)	Yield[b] (%)	Z/E[c]
1	$(Me_3Si)_3SiH$	–	THF	60	48	NR	–
2	$(Me_3Si)_3SiH$	air (2 mL)	THF	r.t.	2	87	98/2
3[d]	$(Me_3Si)_3SiH$	–	THF	70	48	24	98/2
4[d]	$(Me_3Si)_3SiH$	–	THF	r.t.	2	40	98/2
5	$(Me_3Si)_3SiH$	Air (2 mL)	Toluene	r.t.	2	86	98/2
6	$(Me_3Si)_3SiH$	Air (2 mL)	H_2O	r.t.	1	86	98/2
7	$(Me_3Si)_3SiH$	Air (2 mL)	Solvent-free	r.t.	0.5	93	99/1
8	$(Me_3Si)_3SiH$	Air (2 mL)	Solvent-free	0	1	82	98/2
9	$(Me_3Si)_3SiH$	Air (0.5 mL)	Solvent-free	r.t.	1	79	98/2
10	$(Me_3Si)_3SiH$	Air (8 mL)	Solvent-free	r.t.	0.5	71	98/2
11	$(Me_3Si)_3SiH$	Dioxygen (0.5 mL)	Solvent-free	r.t.	0.5	89	98/2
12	$(Me_3Si)_3SiH$	Dioxygen (8 mL)	Solvent-free	r.t.	0.5	65	98/2
13	$(EtO)_3SiH$	Air (2 mL)	Solvent-free	60	12	NR	–
14	Et_3SiH	Air (2 mL)	Solvent-free	60	12	NR	–
15	Ph_2MeSiH	Air (2 mL)	Solvent-free	60	12	NR	–

[a] Reaction conditions: phenylacetylene (1.0 mmol), silane (1.1 mmol), solvent (2 mL) in argon atmosphere.
[b] Isolated yield.
[c] Determined by GC–MS.
[d] In air atmosphere.

Table 2
Air-initiated addition of (TMS)$_3$SiH to terminal alkynes[a]

$$R\!\!=\!\!= + (TMS)_3SiH \xrightarrow[\text{sovlent-free}]{\text{argon/air}} \underset{Z}{R \diagup\!\!\diagdown Si(TMS)_3} + \underset{E}{R \diagup\!\!\diagdown Si(TMS)_3}$$

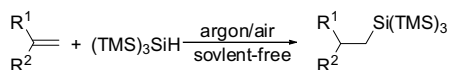| Entry	R	Time (h)	Yield (%)[b]	Z/E[c]
1	C_6H_5	0.5	93	99/1
2	$p\text{-MeC}_6H_4$	1	91	99/1
3	$p\text{-F, }m\text{-MeC}_6H_3$	1	90	99/1
4	$p\text{-amylC}_6H_4$	1	90	99/1
5	1-Cyclohexenyl	3	86	99/1
6[d]	$p\text{-}^tBuC_6H_4OCH_2$	6	80	82/18
7[d]	$C_6H_5CH_2OCH_2$	6	65	99/1
8[d]	$C_6H_5CH(OH)$	6	55	99/1
9	$CH_3(CH_2)_4CH_2$	2	83	82/18
10	$CH_3CH_2CH_2CH_2$	2	86	70/30
11[d]	$HCCCH_2CH_2CH_2$	6	75	98/2

[a] Reaction conditions: alkyne (1.0 mmol), (TMS)$_3$SiH (1.1 mmol) and air (2 mL) in argon atmosphere at room temperature.
[b] Isolated yield.
[c] Determined by GC–MS.
[d] The reaction was carried out at 60 °C.

Table 3
Air-initiated addition of (TMS)$_3$SiH to alkenes[a]

$$\underset{R^2}{\overset{R^1}{>}}\!\!= + (TMS)_3SiH \xrightarrow[\text{sovlent-free}]{\text{argon/air}} \underset{R^2}{\overset{R^1}{|}}\!\!-\!Si(TMS)_3$$

Entry	Alkenes	Time (h)	Isolated yield (%)[b]
1	Styrene	2	79
2[c]	Styrene	2	76
3[d]	Styrene	2	0
4	α-Methylstyrene	6	74
5	p-Methylstyrene	4	73
6	p-Fluorostyrene	4	76
7	1-Decene	6	75
8	Allyl phenyl ether	6	77

[a] Reaction conditions: alkene (1.0 mmol), (TMS)$_3$SiH (1.1 mmol) and air (2.0 mL) in argon atmosphere at 60 °C.
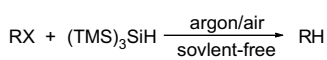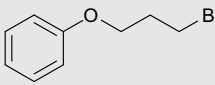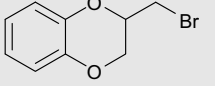[b] Isolated yield.
[c] H_2O as solvent.
[d] The reaction was carried out under pure argon.

Table 4
Air-initiated dehalogenation of halohydrocarbons[a]

$$RX + (TMS)_3SiH \xrightarrow[\text{sovlent-free}]{\text{argon/air}} RH$$

Entry	RX	GC-yield (%)
1	$CH_3(CH_2)_9Br$	87
2[b]	$CH_3(CH_2)_9Br$	0
3[c]	$CH_3(CH_2)_9Br$	26
4	$CH_3(CH_2)_5Br$	81
5	$CH_3(CH_2)_{11}Br$	89
6	$PhCH_2Br$	91
7	$PhBr$	49
8	$BrCH_2COOCH_2CH_3$	76
9	(structure: phenoxy-propyl bromide)	80
10	(structure: benzodioxane-methyl bromide)	86
11	PhI	85
12[d]	PhI	84
13	$PhCH_2Cl$	55
14	Chlorocyclohexane	36
15	$PhCl$	<5

[a] Reaction conditions: halohydrocarbon (1.0 mmol), (TMS)$_3$SiH (1.1 mmol) and air (2.0 mL) in argon atmosphere at 60 °C for 6 h.
[b] The reaction was carried out under pure argon.
[c] The reaction was carried out under air without sealing the vial.
[d] H_2O as solvent.
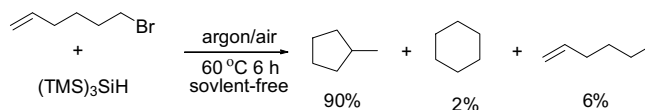
Scheme 1.

cates that the present dehalogenation reaction proceeded via a radical chain pathway (Scheme 1).

Chatgilialoglu has demonstrated that reaction of (TMS)$_3$SiH with adventitious dioxygen could lead to the generation of (TMS)$_3$Si· radical [8,11]. Based on the results described above, these reactions were considered to proceed by a radical mechanism. The initiation step included an autoxygenation reaction of (TMS)$_3$SiH by in situ dioxygen and a hydrogen abstraction reaction to generate a silyl radical. The air-induced radical mechanism is supported by the two facts that all the reactions are retarded by addition of a radical inhibitor, such as 1,4-benzoquinone, and that no reactions take place under pure argon.

3. Conclusion

We have demonstrated that air is also a highly promising initiator for the solvent-free hydrosilylation of unactivated alkynes and alkenes as well as the solvent-free dehalogenation of halohydrocans by (TMS)$_3$SiH with their good selectivity and yields. These reactions are clean, simple, economic, highly efficient, and environmentally friendly, as just the addition of a catalytic amount of air is required, which avoids the need for a special workup procedure and makes this method compatible with sensitive, highly functionalized molecules. The results obtained in this work should provide useful data for the design of new silyl radical chain reactions in organic synthesis. Further development on this methodology is currently under way in our laboratory.

shown in Table 4, the reaction is general for different organic halides, and in most cases gives the corresponding dehalogenated products in moderate to excellent yields. Generally, chlorides, bromides, and iodides tend to display an increasing reactivity in the order of RCl < RBr < RI, which may be envisaged from their overall behavior in Table 4 (Table 4, entries 7, 11 and 15). And for a particular halogen atom, aryl halides were less reactive toward (TMS)$_3$SiH than alkyl halides (Table 4, entries 5 and 7). A (TMS)$_3$SiH/O$_2$-promoted coupling reaction of aryl iodides with arenes was recently reported [16]. However, in that case O$_2$ is stoichiometric as a H-acceptor and plays a different role. All these demonstrate the potential of diverse applications of silanes/dioxygen system in organic synthesis. Significantly, the presence of functionalities such as ester or ether groups in the starting materials did not interfere with the outcome of the reaction (Table 4, entries 8–10). The results represent the first example of air-induced dehalogenatation under solvent-free condition.

To explore the scope, we also examined the reaction of 6-bromo-1-hexene. As expected, this reaction gave the methylcyclopentane as the major product together with a small amount of cyclohexane and simple reduction product [17]. This further indi-

4. Experimental

All silanes, alkynes and alkenes were purchased from Aldrich. The ^{1}H NMR spectra were recorded in CDCl$_3$ on a Bruker AV 400 (400 MHz for ^{1}H) spectrometer. ^{13}C NMR spectra were recorded in CDCl$_3$ on a Bruker AV 400 (100 MHz for ^{13}C) with TMS as the internal standard with complete decoupling. Chemical shifts are reported in ppm, and J values are given in Hz. GC-MS were obtained on a Hewlett–Packard 6890/5973 instrument.

4.1. General procedure for the addition of (TMS)$_3$SiH to alkynes

To a 10 mL vial was added alkynes (1.0 mmol) and (TMS)$_3$SiH (1.1 mmol) under argon, then 2 mL air was introduced into the vial via syringe. The vial was sealed, and then the mixture was stirred at the corresponding temperature for 0.5–6 h. After completion of the reaction (monitored by TLC), the reaction of mixture was purified by flash chromatographed on silica gel using hexane/ethyl acetate as the eluent. All products were identified by comparison of their ^{1}H NMR and MS spectra with those of authentic samples [13], or showed satisfactory analytical data and expected spectra.

4.2. (Z)-1-(p-Tolyl)-2-[tris(trimethylsilyl)silyl]ethene

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.37 (d, 1H, J = 14.5 Hz), 7.22 (d, 2H), 7.08 (d, 2H), 5.82 (d, 1H, J = 14.5 Hz), 2.30 (s, 3H), 0.12 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.63, 137.80, 132.16, 129.17, 128.09, 123.06, 21.38, 1.41. GC–MS m/z: 364 (M$^+$), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.3. (Z)-1-(4-Fluoro-3-methylphenyl)-2-[tris(trimethylsilyl)silyl]ethene

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.32 (d, 1H, J = 14.5 Hz), 7.14 (s, 1H), 6.93–7.08 (m, 2H), 5.83 (d, 1H, J = 14.5 Hz), 2.27 (s, 3H), 0.12 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 162.03, 159.57, 145.78, 136.70, 131.20, 126.87, 124.67, 123.97, 114.84, 14.64, 1.36. GC/MS m/z: 382 (M$^+$), 174 ((TMS)$_2$Si)$^+$, 73(TMS)$^+$.

4.4. (Z)-1-(p-Amylphenyl)-2-[tris(trimethylsilyl)silyl]ethene

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.46 (d, 1H, J = 14.2 Hz), 7.30 (d, 2H, J = 7.32 Hz), 7.16 (d, 2H, J = 7.32 Hz), 5.90 (d, 1H, J = 14.2 Hz), 2.64 (t, J = 7.56 Hz, 2H), 1.60–1.69 (m, 2H), 1.30–1.38 (m, 4H), 0.94 (t, J = 7.32 Hz, 3H), 0.12 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.72, 142.14, 138.22, 128.50, 128.03, 123.30, 35.82, 31.49, 31.36, 22.71, 14.22, 1.42. GC/MS m/z: 420 (M$^+$), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.5. (Z)-1-(1-Cyclohexenyl)-2-[tris(trimethylsilyl)silyl]ethene

^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.67 (d, 1H, J = 14.3 Hz), 5.74 (t, 1H), 5.40 (d, 1H, J = 14.3 Hz), 2.07–2.13 (m, 4H), 1.58–1.68 (m, 4H), 0.17 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 149.42, 138.92, 124.95, 118.61, 28.47, 25.38, 22.61, 22.13, 1.33. GC/MS m/z: 354 (M$^+$), 174 ((TMS)$_2$Si)$^+$, 73(TMS)$^+$.

4.6. 1-[Tris(trimethylsilyl)]allyl 4-^{t}butylphenyl ether

^{1}H NMR (CDCl$_3$, 400 MHz) Z-isomer δ 7.35 (d, 2H, J = 8.7 Hz), 6.90 (d, 2H, J = 8.7 Hz), 6.73–6.78 (m, 1H), 5.98 (d, 1H, J = 13.3 Hz), 4.55 (d, 2H, J = 6.4 Hz), 1.36 (s, 9H), 0.15 (s, 27H). E-isomer δ 7.35 (d, 2H, J = 8.7 Hz), 6.90 (d, 2H, J = 8.7 Hz), 6.53–6.61 (m, 1H), 5.70 (d, 1H, J = 18.3 Hz), 4.76 (d, 2H, J = 6.3 Hz), 1.36 (s,

9H), 0.15 (s, 27H). GC/MS m/z: 436 (M$^+$), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.7. (Z)-3-Benzyloxyl-1-[tris(trimethylsilyl)]-1-propene

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30–7.40 (m, 5H), 6.54–6.61 (m, 1H), 5.80 (d, 1H, J = 13.6 Hz), 4.54 (s, 2H), 4.04 (d, 2H, J = 6.3 Hz), 0.14 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 144.78, 138.89, 128.55, 128.50, 128.22, 124.55, 72.99, 71.63, 0.94. GC/MS m/z: 321 (M$^+$−73), 73 (TMS)$^+$.

4.8. (Z)-1-Phenyl-3-[tris(trimethylsilyl)]allyl alcohol

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30–7.40 (m, 5H), 6.55–6.60 (m, 1H), 5.90 (d, 1H, J = 13.3 Hz), 5.16 (d, 1H, J = 9.2 Hz), 1.74 (br 1H), 0.13 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 148.17, 142.85, 130.04, 128.66, 126.67, 124.57, 67.54, 1.53. GC/MS m/z: 378 (M$^+$−2), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.9. (Z)-1-[Tris(trimethylsilyl)silyl]-1-heptene-6-yne

^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.34-6.40 (m, 1H), 5.54 (d, 1H, J = 12.8 Hz), 2.20-2.26 (m, 4H), 1.93 (t, 1H, J = 2.7 Hz), 1.60–1.65 (m, 2H), 0.14 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 148.06, 121.26, 82.24, 68.17, 34.58, 28.22, 18.51, 1.30. GC/MS m/z: 340 (M$^+$), 267 (M$^+$−73), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.10. General procedure for the addition of (TMS)$_3$SiH to alkenes

To a 10 mL vial was added alkenes (1.0 mmol) and (TMS)$_3$SiH (1.1 mmol) under argon, then 2 mL air was introduced into the vial via syringe. The vial was sealed, and then the mixture was stirred at 60 °C for 2–6 h. After the completion of the reaction (monitored by TLC), the reaction of mixture was purified by flash chromatography on silica gel using hexane/ethyl acetate as the eluent.

4.11. 1-(p-Tolyl)-2-[tris(trimethylsilyl)silyl]ethane

^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.92–7.12 (m, 4H), 2.62–2.66 (m, 2H), 2.34 (s, 3H), 1.06–1.10 (m, 2H), 0.21 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 129.21, 129.00, 127.56, 127.31, 35.19, 21.20, 10.92, 1.45. GC/MS m/z: 366 (M$^+$), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.12. 1-(p-Fluorophenyl)-2-[tris(trimethylsilyl)silyl]ethane

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.12–7.14 (m, 2H), 6.95–6.98 (m, 2H), 2.64–2.67 (m, 2H), 1.07–1.11 (m, 2H), 0.24 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 162.35, 128.98, 128.91, 115.25, 34.77, 10.88, 1.38. GC/MS m/z: 370 (M$^+$), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.13. Phenyl 3-[tris(trimethylsilyl)]propyl ether

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.24–7.27 (m, 2H), 6.85–6.92 (m, 3H), 3.89 (t, 2H, J = 6.8 Hz,), 1.83–1.87 (m, 2H), 0.86–0.90 (m, 2H), 0.15 (s, 27H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 159.18, 129.51, 120.57, 114.63, 70.70, 28.82, 3.69, 1.30. GC/MS m/z: 382 (M$^+$), 315 (M$^+$−73), 174 ((TMS)$_2$Si)$^+$, 73 (TMS)$^+$.

4.14. General procedure for the dehalogenation of halohydrocarbons by (TMS)$_3$SiH

To a 10 mL vial was added halohydrocarbons and (TMS)$_3$SiH under argon, then 2 mL air was introduced into the vial via syringe. The vial was sealed and heated at 60 °C for 6 h and then analyzed

by GC–MS. Yields were quantified by GC using dodecane or decane as an internal standard.

Acknowledgements

References

[1] (a) C. Chatgilialoglu, Organosilanes in Radical Chemistry, Wiley, Chichester, 2004 (Chapter 5);
(b) J.A. Reiche, D.H. Bery, Adv. Organomet. Chem. 43 (1998) 197;
(c) G.A. Molander, J.A.C. Romero, Chem. Rev. 102 (2002) 2161;
(d) E. Barnea, M.S. Eisen, Coord. Chem. Rev. 250 (2006) 855.
[2] (a) M. Ballestri, C. Chatgilialoglu, K.B. Clark, D. Griller, B. Giese, B. Kopping, J. Org. Chem. 56 (1991) 678;
(b) C. Chatgilialoglu, T. Gimisis, Chem. Commun. (1998) 1249;
(c) C.L. Mero, N.A. Porter, J. Am. Chem. Soc. 121 (1999) 5155;
(d) D.C. Harrowven, T. Woodcock, P.D. Howes, Angew. Chem., Int. Ed. 44 (2005) 3899.
[3] (a) M. Newcomb, S.U. Park, J. Am. Chem. Soc. 108 (1986) 4132;
(b) C. Chatgilialoglu, Acc. Chem. Res. 25 (1992) 188;
(c) B.C. Gilbert, A.F. Parson, J. Chem. Soc., Perkin Trans. II (2002) 367;
(d) A. Studer, S. Amrein, Synthesis (2002) 835.
[4] (a) C.S. Aricó, L.R. Cox, Org. Biomol. Chem. 2 (2004) 2558;
(b) K.A. Horn, Chem. Rev. 95 (1995) 1317.
[5] M. Oba, M. Suyama, A. Shimamura, K. Nishiyama, Tetrahedron Lett. 44 (2003) 4027.
[6] (a) M.G. Steinmetz, R.T. Mayes, B.S. Udayakumar, J. Chem. Soc., Chem. Commun. (1987) 759;
(b) F. Wang, D.C. Neckers, J. Organomet. Chem. 665 (2003) 1.
[7] P.A. Baguley, J.C. Walton, Angew. Chem., Int. Ed. 37 (1998) 3072. and references therein.
[8] C. Chatgilialoglu, A. Guarini, A. Guerrini, G. Seconi, J. Org. Chem. 57 (1992) 2207.
[9] (a) Y. Liu, S. Yamazaki, S. Yamabe, J. Org. Chem. 70 (2005) 556;
(b) Y. Liu, S. Yamazaki, S. Yamabe, Y. Nakato, J. Mater. Chem. 15 (2005) 4906;
(c) Y. Liu, S. Yamazaki, S. Izuhara, J. Organomet. Chem. 691 (2006) 5809.
[10] (a) Z.Y. Zhu, C.W. Wang, X. Xiang, C.F. Pi, X.G. Zhou, Chem. Commun. 19 (2006) 2066;
(b) Z.Y. Zhu, J.L. Wang, Z.X. Zhang, X. Xiang, X.G. Zhou, Organometallics 26 (2007) 2499.
[11] (a) A.B. Zaborovskiy, D.S. Lutsyk, R.E. Prystansky, V.I. Kopylets, V.I. Timokhin, C. Chatgilialoglu, J. Organomet. Chem. 689 (2004) 2912;
(b) C. Chatgilialoglu, A. Guerrini, M. Lucarini, G.F. Pedulli, P. Carrozza, G.D. Roit, V. Borzatta, V. Lucchini, Organometallics 17 (1998) 2169.
[12] (a) A. Postigo, C. Ferreri, M.L. Navacchia, C. Chatgilialoglu, Synlett (2005) 2854;
(b) A. Postigo, S. Kopsov, C. Ferreri, C. Chatgilialoglu, Org. Lett. 9 (2007) 5159.
[13] B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, J. Org. Chem. 57 (1992) 3994.
[14] (a) B.M. Trost, Z.T. Ball, K.M. Laemmerhold, J. Am. Chem. Soc. 127 (2005) 10028;
(b) B.M. Trost, Z.T. Ball, J. Am. Chem. Soc. 127 (2005) 17644;
(c) B.M. Trost, Z.T. Ball, T. Jöge, Angew. Chem., Int. Ed. 42 (2003) 3415.
[15] F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 102 (2002) 4009, and references therein.
[16] D.P. Curran, A.I. Keller, J. Am. Chem. Soc. 128 (2006) 13706.
[17] C. Chatgilialoglu, D. Griller, M. Lesage, J. Org. Chem. 53 (1988) 3641.