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SILAFUNCTIONAL COMPOUNDS IN ORGANIC SYNTHESIS

XVIII *. OXIDATIVE CLEAVAGE OF THE SILICON–CARBON BOND IN ALKENYLFLUOROSILANES TO CARBONYL COMPOUNDS: SYNTHETIC AND MECHANISTIC ASPECTS

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Summary

Alkenyltrifluorosilanes are readily oxidized by one equivalent of MCPBA in DMF even at −50°C to give the corresponding carbonyl compounds via cleavage of the carbon–silicon bond. With three equivalent of MCPBA a concomitant cleavage of the carbon–carbon bond occurs. A plausible mechanism of these new types of oxidation has been discussed. Oxidation with DABCO · $2H_2O_2$ has also been described.

Introduction

We have recently recognized that the functional silyl group is synthetically equivalent to the hydroxyl group (eq. 1) [1]. For example, alkyl-pentafluorosilicates and -fluorosilanes undergo the *m*-chloroperbenzoic acid (MCPBA) cleavage of the carbon–silicon bond to form the corresponding alcohols in high yields.

$$\text{R}-si \xrightarrow[\text{DMF}]{\text{MCPBA}} \text{R}-\text{OH} \quad (1)$$

si = fluorosilyl group

We describe herein the similar oxidative cleavage of alkenyltrifluorosilanes to form carbonyl compounds, together with some mechanistic aspects which suggest the reaction to involve the direct oxidative cleavage of the carbon–silicon bond (eq. 2), unlike the oxidation of the trimethylsilyl counterparts, which requires a sequence of epoxidation and acidolysis (eq. 3) [2].

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[*] For part XVII, see ref. 1a. The present, new series has been numbered consecutively from the previous one entitled "Organofluorosilicates in Organic Synthesis".

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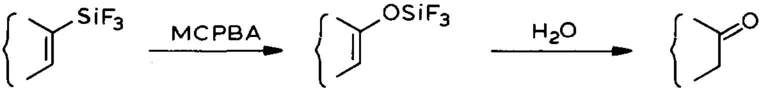

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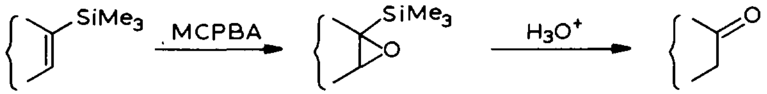

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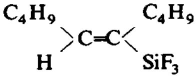
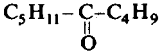
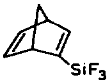
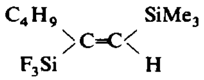
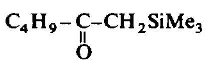
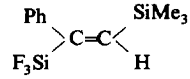
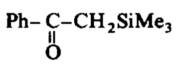
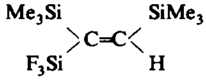
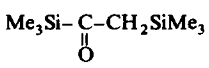
Results and discussion

MCPBA oxidation of alkenyltrifluorosilanes: synthetic utility

Alkenyltrifluorosilanes react readily with one equivalent of MCPBA in DMF even at −50°C; they are much more reactive than alkyltrifluorosilanes. Only the hydrolysis work-up gives the corresponding carbonyl compounds. The carbonyl group appears at the carbon originally bearing silicon. Several representative results are listed in Table 1. The present method has opened up a new route from acetylenes to carbonyl compounds via a sequence of hydrosilylation-oxidation, similar to the hydroboration-oxidation sequence [3] (entries 1–3). The present procedure also provides a single-step conversion of a cyclic vinylsilane to the corresponding cyclic ketone, while the traditional transformation of a cyclic vinylic trimethylsilane (eq. 3)

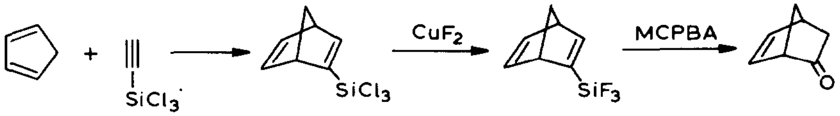
TABLE 1

MCPBA CLEAVAGE OF ALKENYLTRIFLUOROSILANES IN DMF [a]

Alkenyltrifluorosilane	Product	Yield [b] (%)
(E)-$C_6H_{13}CH{=}CHSiF_3$	$C_7H_{15}CHO$	82 (95)
(E)-$PhCH{=}CHSiF_3$	$PhCH_2CHO$	(75)
 $(C_4H_9)(H)C{=}C(C_4H_9)(SiF_3)$	 $C_5H_{11}-C(=O)-C_4H_9$	76
		(56)
 $(C_4H_9)(F_3Si)C{=}C(SiMe_3)(H)$	 $C_4H_9-C(=O)-CH_2SiMe_3$	56 [c]
 $(Ph)(F_3Si)C{=}C(SiMe_3)(H)$	 $Ph-C(=O)-CH_2SiMe_3$	60 [c]
 $(Me_3Si)(F_3Si)C{=}C(SiMe_3)(H)$	 $Me_3Si-C(=O)-CH_2SiMe_3$	48 [c]

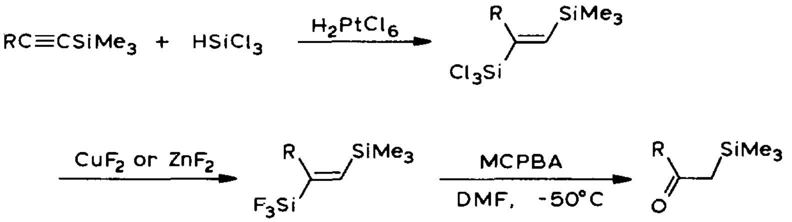
[a] A mixture of $RSiF_3$ (3 mmol), MCPBA (80 or 93% purity, 3 mmol), and dry DMF was stirred at −50°C for 1 h and hydrolyzed. [b] Isolated yield. Yields given in parentheses were determined by GLC. [c] Desilylated methyl ketones were also formed in 6–24% yields.

does not usually lead to the expected carbonyl compound because of stereochemical restrictions [4]. In this way, 5-norbornen-2-one, versatile synthetic intermediate [5], has been prepared from the Diels–Alder adduct of ethynyltrichlorosilane with cyclopentadiene [6] (entry 4 and eq. 4).



(4)

The present cleavage occurs selectively at the carbon–SiF_3 bond keeping the carbon–$SiMe_3$ bond intact. Thus, α-trimethyl silyl ketones [7] are prepared by this method in conjunction with hydrosilylation of silylacetylenes [8], as shown by eq. 5 and data in Table 1. Although substantial amounts of methyl ketones are also formed as secondary products as a result of the solvolysis of α-silyl ketones, the present method provides a new route to α-silyl ketones, which are versatile synthetic intermediates such as a vinyl cation equivalent [9]. [(Trimethylsilyl)acetyl]trimethylsilane reported here has already been prepared by hydroboration of bis(silyl)acetylene [10] and used in a stereoselective olefin synthesis [11].



(5)

Brief comments on the preparation of alkenylfluorosilanes

The starting materials, alkenyltrifluorosilanes, are readily available from the corresponding chlorosilanes by treatment with stoichiometric amounts of $CuF_2 \cdot 2H_2O$ (eq. 6) [1a]. In certain cases, however, this method gave nonvolatile polysiloxanes mainly rather than the trifluorosilanes, and ZnF_2 was used in the conventional way [12] (see Experimental).

$$R\text{–}SiCl_3 + 1.5CuF_2 \rightarrow R\text{–}SiF_3 + 1.5CuCl_2 \qquad (6)$$

For the preparation of styryltrifluorosilane, care must be taken to use exactly the stoichiometric amount of CuF_2, since an excess amount of CuF_2 results in the formation of styryl chloride. It seems likely that the initially formed styryltrifluorosilane is converted by the action of CuF_2 to a "copper(II) styrylpentafluorosilicate" species which reacts with $CuCl_2$ present in the reaction mixture to give styryl chloride, together with copper(I) chloride and hexafluorosilicate [13]. The overall stoichiometry may be written as eq. 7.

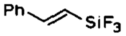
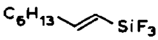
(7)

Mechanistic aspects

The yields of carbonyl compounds and the reaction courses are dependent upon the nature of the solvent, the reaction temperature, and the amount of the oxidant.

TABLE 2

PRODUCT DISTRIBUTION IN MCPBA CLEAVAGE OF ALKENYLTRIFLUOROSILANES

Entry	MCPBA (equiv)	Conditions[a]	Yield[b] (%)	
		→	PhCHO	$PhCH_2CHO$
1	1	DMF/−50°C/1 h	0	74
2	1	DMF/0°C/1 h	10	53
3	1	THF/−50°C/1 h	trace	trace
4	1	THF/DMF (1 eq)/−50°C/1 h	trace	trace
5	1	THF/HMPA (1 eq)/−50°C/1 h	8	32
6	3[c]	DMF/−50°C ~ r.t./2 h	49	trace
7	3[c]	DMF/−50°C ~ +70°C/2.5 h	65	0
8	3[c]	THF/−50°C ~ r.t./2 h	63	0
		→	$C_6H_{13}CHO$	$C_6H_{13}CH_2CHO$
9	1	DMF/−50°C/1 h	0	95
10	1	THF/DMF (1 eq)/0°C/0.5 h	3	49
11	1	THF/DMF (1 eq)/r.t./3 h	30	trace
12	2[d]	THF/DMF (1 eq)/r.t./5 h	43	trace
13	3[c]	THF/DMF (1 eq)/rfx./1 h	37	12
14	3[c]	DMF/−50°C ~ r.t./3 h	44	18

[a] Carried out on a 1 mmol scale in 5 ml of the given solvent. [b] Determined by GLC. [c] Added in three portions. [d] Added in two portions.

Table 2 summarizes results observed with octenyl- and styryl-trifluorosilane. In contrast to the clean reaction at −50°C in DMF mentioned above, all the other conditions employed here gave rise to the concomitant or exclusive formation of an aldehyde having one-carbon less as a result of the carbon–carbon bond cleavage (eq. 8).

(8)

Results observed with styrylsilane are most informative. While no reaction occurred in THF (entry 3), addition of one equiv of HMPA facilitated the reaction, but benzaldehyde was formed as a by-product. Higher temperature also caused the formation of benzaldehyde (entry 2). The use of three equivalent of MCPBA resulted in the exclusive formation of benzaldehyde (entries 6–8). Similar results have been obtained with octenyltrifluorosilane.

GLC monitoring of the reaction of styryltrifluorosilane clearly indicated that benzaldehyde is the secondary product of the primary product phenyl acetaldehyde. As shown in Fig. 1, the yield of benzaldehyde increases at each point (shown by three arrows) of addition of one more equivalent of MCPBA at the expense of the initially formed phenyl acetaldehyde.

The oxidation also depends on the number of fluorines on silicon, as observed with a styrylsilane series, the results being summarized in Table 3. The reactivity decreases steadily with decreasing number of fluorines. The trifluorosilane is most reactive, the difluoromethylsilane reacts at 0°C to form benzaldehyde predomi-

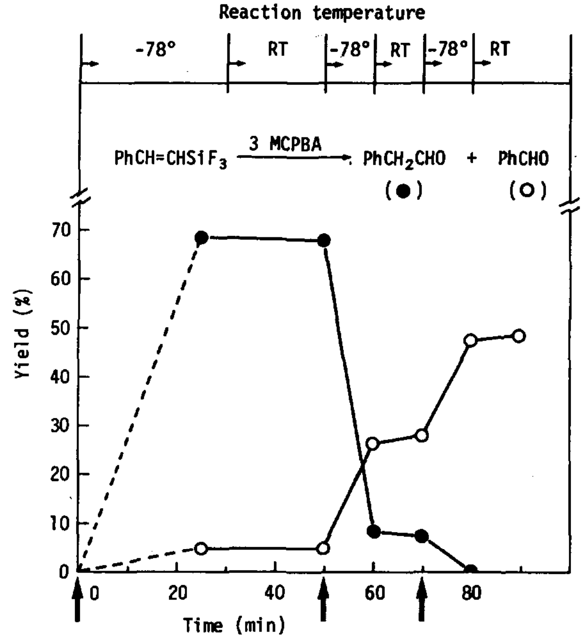


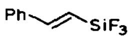
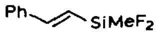
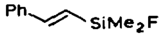
Fig. 1. GLC-monitoring of the oxidation of (*E*)-styryltrifluorosilane with three equiv of MCPBA in THF containing five equiv of DMF. MCPBA was added in three portions (one equiv each), as shown by three arrows. RT denotes room temperature.

nantly, and no reaction is observed with the monofluorodimethylsilane, the starting material being recovered.

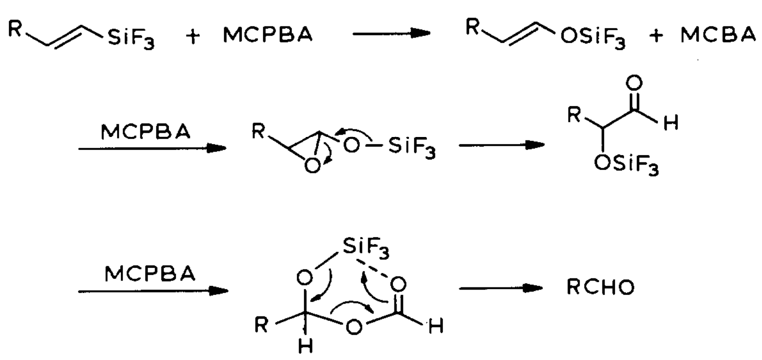
The fact that the most electron-withdrawing trifluorosilyl group [14] facilitates the oxidation strongly suggests that the present oxidation is not initiated by epoxidation of the olefin, but involves the direct oxidation of the silicon–carbon bond to form an enol silyl ether as the initial product. This initial step may proceed through penta- and hexa-coordinate silicon species, as proposed previously for oxidation of the alkyl–silicon bond in alkyltrifluorosilanes [1a].

TABLE 3

MCPBA CLEAVAGE OF A SERIES OF STYRYLFLUOROSILANES[a]

Styrylsilane	Conditions	Products, Yield[b] (%)	
		PhCHO	$PhCH_2CHO$
	−50°C/1 h	0	75
	−50°C/1.5 h 0°C/1 h	3 36	3 4
	r.t./2 h	no reaction	

[a] Carried out on a 1 mmol scale in DMF with one equiv of MCPBA. [b] Determined by GLC.



SCHEME 1

A plausible mechanism for the whole reaction is shown in Scheme 1. The alkenyltrifluorosilane is converted to the enol silyl ether by the first one equivalent of MCPBA. Work-up at this stage results in the formation of the carbonyl compounds having the same number of carbon atoms. Another equivalent of MCPBA epoxidizes the resulting enol silyl ether intermediate which contains an electron-rich olefin susceptible to the attack of MCPBA. The epoxide may rearrange to an α-siloxycarbonyl compound. The subsequent Baeyer–Villiger oxidation of this intermediate by the third one equivalent of MCPBA results in the cleavage of the carbon–carbon bond to form an aldehyde of one-carbon less than the initial aldehyde. The stoichiometry of the overall reaction may be written as eq. 9, although the silyl formate species could not be detected.

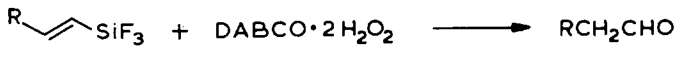
$$\mathrm{RCH{=}CHSiF_3 + 3MCPBA \rightarrow RCHO + [HCOOSiF_3] + 3MCBA} \qquad (9)$$

The proposed mechanism is supported by the precedents in the literature. Thus, the MCPBA oxidation of enol silyl ethers has been reported to form α-siloxy ketones [15] and also undergo the carbon–carbon bond cleavage of the latter with an excess amount of MCPBA [16].

Finally, in connection with the first oxidation step in the present system, it should be noted that the so-far reported transformation of alkenyltrimethylsilanes into the corresponding enol silyl ethers by treatment with ozone [17] or a nitrile oxide [18], is mechanistically quite different from our present oxidation, since in those cases the oxidizing agent interacts preferentially with the carbon–carbon double bond rather than the silicon center.

Hydrogen peroxide oxidation of alkenyltrifluorosilanes

Alkenyltrifluorosilanes are oxidized to carbonyl compounds also by a complex [19] of hydrogen peroxide with DABCO (1,4-diazabicyclooctane) (eq. 10 and Table 4). The yields are not necessarily very high, but this reaction affords the first example of the hydrogen peroxide oxidation of the silicon–carbon bond and also provides a strong support for the direct oxidation of the silicon–carbon bond mentioned above, in view of the low ability of hydrogen peroxide in epoxidation.

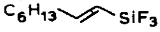
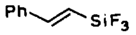


(10)

In connection with this reaction, we have quite recently found that the

TABLE 4

OXIDATION OF ALKENYLTRIFLUOROSILANES WITH DABCO·$2H_2O_2$ [a]

$RCH=CHSiF_3$	Conditions	Yield (%) [b] RCH_2CHO
	DMF/−50°C/1 h	46
	DMF/r.t./1 h	47
	DMF/r.t./1 h [c]	49
	DMF/−50°C/1 h	57
	THF/r.t./1 h	35
	THF/r.t./1 h	44

[a] One equiv of DABCO·$2H_2O_2$ was used, unless otherwise stated. [b] Determined by GLC. [c] Two equiv of DABCO·$2H_2O_2$ were used.

carbon–silicon bond in organo(alkoxy)silanes is readily cleaved even by 30% hydrogen peroxide in the presence of fluoride ions. The results will be reported elsewhere shortly.

Experimental

General

^1H NMR, IR, MS, and GLC facilities have been described in our previous paper [20]. The NMR spectra were taken in a CCl_4 solution. Hydrolyzable chlorine in the starting materials was determined by the usual double titration method within ±0.4% errors.

Hydrosilylation of acetylenes

Hydrosilylation of 1-octyne, phenylacetylene, and 5-decyne was carried out in the usual manner in the presence of $H_2PtCl_6 \cdot 6H_2O$ as a catalyst [20].

(E)-1-Trimethylsilyl-2-trichlorosilyl-1-hexene. A mixture of 1-trimethylsilyl-1-hexyne and trichlorosilane (ca. 1.2 equiv) was refluxed in the presence of $H_2PtCl_6 \cdot 6H_2O$ as a catalyst (a few drops of 0.1 *M* solution in 2-propanol) for 6 h. Distillation gave the title compound in 97% yield: b.p. 116°C/16 Torr. ^1H NMR: δ 0.20 (s, 9H), 0.85–1.05 (m, 3H), 1.2–1.7 (m, 4H), 2.35–2.60 (m, 2H), 6.65 (s, 1H). The procedure is essentially the same as the literature method [8].

(E)-1-Phenyl-1-trichlorosilyl-2-trimethylsilylethene. This compound was obtained in the same manner, except for 11 h-refluxing, in 91% yield: b.p. 99°C/4 Torr. ^1H NMR: δ −0.12 (s, 9H), 7.0–7.4 (m, 6H). An aliquot (0.51 g) was methylated with the methyl Grignard reagent to give (*E*)-1-phenyl-1,2-bis(trimethylsilyl)ethene in 71% yield: b.p. 116°C/16 Torr. The spectra were superimposable with those of the previously reported compound obtained via double silylation of phenylacetylene [21].

1-Trichlorosilyl-1,2-bis(trimethylsilyl)ethene. A prolonged reaction time was necessary to obtain the title compound by the addition of trichlorosilane to 1,2-bis(trimethylsilyl)acetylene catalysed by $H_2PtCl_6 \cdot 6H_2O$. After 80 h-refluxing, distillation gave the product in 23% yield: b.p. 95–105°C/13 Torr (bath temperature). ^1H NMR: δ 0.27 (s, 9H), 0.33 (s, 9H), 7.90 (s, 1H). The stereochemistry has been assigned tentatively to be (*E*), based on the usual *cis* hydrosilylation.

Preparation of fluorosilanes

A general procedure for the reaction of organochlorosilanes with $CuF_2 \cdot 2H_2O$ has already been described in our previous paper [1a]. Described herein is only a typical procedure for the preparation of alkenyltrifluorosilanes by use of $ZnF_2 \cdot 4H_2O$.

5-Trifluorosilyl-5(E)-decene. 5-Trichlorosilyl-5(*E*)-decene (4.1 g; 15 mmol) was added dropwise to powdered $ZnF_2 \cdot 4H_2O$ (26.3 g; 150 mmol) with occasional shaking at room temperature. An exothermic reaction occurred and a clear liquid phase and a creamy heavier layer resulted. The product was extracted several times with pentane by decantation and dried over Na_2SO_4. After evaporation of the solvent bulb-to-bulb distillation gave 2.6 g (75% yield) of 5-trifluorosilyl-5(*E*)-decene boiling over the range of 65–80°C/24 Torr (bath temperature); ^1H NMR 0.8–1.1 (t, 6H), 1.2–1.7 (m, 8H), 2.1–2.4 (m, 4H), 6.43 (t, J 7 Hz, 1H). Found: F, 25.13. $C_{10}H_{19}F_3Si$ calcd.: F, 25.41%.

Action of excess amounts of $CuF_2 \cdot 2H_2O$ on styryltrichlorosilane

To a stirred mixture of $CuF_2 \cdot 2H_2O$ (5.3 g; 38.5 mmol) in ether was added styryltrichlorosilane (5.0 g; 21.4 mmol) dropwise at 0°C. After stirring at room temperature for 15 h, additional $CuF_2 \cdot 2H_2O$ (3.0 g; 21.8 mmol) was added and stirring was continued for 4 h. Pentane was added and the resulting whitish precipitates were filtered, and washed with pentane. Distillation gave 1.59 g (54% yield) of (*E*)-styryl chloride: b.p. 82–85°C/12 Torr (bath temperature), which was characterized by comparison with the authentic sample. GLC-monitoring of a small scale experiment showed that styryltrifluorosilane was the sole product after 1 h-stirring and it was gradually transformed into styryl chloride and finally, after 6 h-stirring, the latter was formed exclusively in 84% yield by GLC determination.

Yield, boiling point, ^1H NMR data, and fluorine content (F%) of alkenyltrifluorosilanes prepared here are summarized below. Unless otherwise noted, $CuF_2 \cdot 2H_2O$ was used.

(E)-1-Trifluorosilyl-1-octene. 67% yield; b.p. 72–74°C/58 Torr; δ 0.80–1.20 (m, 3H), 1.20–1.75 (br, 8H), 2.16–2.46 (m, 2H), 5.30–5.65 (m, 1H), 6.86 (dt, J 6.5 and 19 Hz, 1H). Found: F, 29.41. $C_8H_{15}F_3Si$ calcd.: F, 29.04%.

(E)-Styryltrifluorosilane. 73% yield; b.p. 61–63°C/15 Torr; δ 5.97–6.24 (m, 1H), 7.1–7.7 (m, 6H). Found: F, 30.91. $C_8H_7F_3Si$ calcd.: F, 30.28%.

(E)-Styrylmethyldifluorosilane. 8% yield; b.p. 86°C/15 Torr; δ 0.49 (t, J 6 Hz, 3H), 6.20 (dt, J 20 Hz, J(HF) 3 Hz, 1H), 7.2–7.6 (m, 6H). Found: F, 20.40. $C_9H_{10}F_2Si$ calcd.: F, 20.62%.

(E)-Styryldimethylfluorosilane. 33% yield; b.p. 102–103°C/16 Torr; δ 0.32 (d, J 7 Hz, 6H), 6.35 (dd, J 20 Hz, J(HF) 3 Hz, 1H), 7.05 (d, J 20 Hz, 1H), 7.20–7.55 (m, 5H). Found: F, 10.38. $C_{10}H_{13}FSi$ calcd.: F, 10.54%.

2-Trifluorosilylnorbornadiene. 27% yield; b.p. 90°C/125 Torr (bath temperature); δ 1.9–2.1 (m, 2H), 3.7–4.1 (m, 2H), 6.4–6.9 (m, 2H), 7.7–8.0 (m, 1H). Found: F, 32.83. $C_7H_7F_3Si$ calcd.: F, 32.35%.

1-Trimethylsilyl-2-trifluorosilyl-1(E)-hexene. 76% yield (ZnF_2); b.p. 120°C/40 Torr (bath temperature); δ 0.13 (s, 9H), 0.80–1.10 (t, 3H), 1.20–1.55 (m, 4H), 2.05–2.40 (m, 2H), 6.29 (s, 1H). Found: F, 24.47. $C_9H_{19}F_3Si_2$ calcd.: F, 23.71%.

(E)-1-Phenyl-1-trifluorosilyl-2-trimethylsilylethene. 69% yield; b.p. 100°C/18 Torr (bath temperature); δ − 0.12 (s, 9H), 6.95–7.45 (m, 6H). Found: F, 21.53. $C_{11}H_{15}F_3Si_2$ calcd.: F, 21.89%.

(E)-1,2-Bis(trimethylsilyl)-1-trifluorosilylethene. 54% yield; 120°C/93 Torr (bath temperature); δ 0.22 (s, 9H), 0.24 (s, 9H), 7.93 (q, J(HF) 1.8 Hz, 1H). Found: F, 22.52. $C_8H_{19}F_3Si_3$ calcd.: F, 22.22%.

MCPBA oxidation of alkenyltrifluorosilanes: A typical procedure

Commercial MCPBA was purified by the established method [22]. To a mixture of 1-octenyltrifluorosilane (796 mg; 4.0 mmol) and dry DMF (20 ml) was added dropwise a solution of MCPBA (purity 93%; 778 mg; 4.2 mmol) in DMF (2 ml) at −50°C. After stirring at the same temperature for 1 h the mixture was poured into a mixture of water and pentane. The organic layer was separated and the aqueous layer was extracted with pentane three times. The combined organic layer and extracts were washed with 10% $NaHSO_3$ (once), saturated $NaHCO_3$ (three times), and water, and dried over Na_2SO_4. Bulb-to-bulb distillation after evaporation of the solvent gave 424 mg (82% yield) of octanal. No other products were detected by GLC. Essentially the same result was obtained with commercial MCPBA of 80% purity.

Reaction of (E)-styryltrifluorosilane with an excess amount of MCPBA: GLC-monitoring

To a mixture of styryltrifluorosilane (184 mg; 0.98 mmol), DMF (373 mg; 5.1 mmol), tridecane (70 mg) as an internal standard, and dry THF (5 ml) was added a solution of MCPBA (80% purity, 242 mg; 1.13 mmol) in THF (1 ml) at −78°C. An aliquot was hydrolyzed and analyzed by GLC, which showed the formation of phenyl acetaldehyde and benzaldehyde. The mixture was warmed up to room temperature and then analyzed by GLC as above. After cooling at −78°C again, the second one equiv of MCPBA (240 mg; 1.12 mmol) in THF was added and the mixture was analyzed. These operations were repeated totally three times. The results are plotted in Fig. 1.

Oxidation with DABCO · $2H_2O_2$: A typical procedure

DABCO · $2H_2O_2$ was prepared by the literature method [19]. To a mixture of (*E*)-octenyltrifluorosilane (195 mg; 1.0 mmol) was added DABCO · $2H_2O_2$ (187 mg; 1.0 mmol) at room temperature. A slighly exothermic reaction occurred. After stirring at room temperature the mixture was poured into water and extracted with ether. GLC analysis (internal standard dodecane) of the organic layer showed the formation of octanal in 49% yield.

Of the oxidation products, octanal, 5-decanone, and phenyl acetaldehyde were characterized by comparison with the authentic samples. ^1H NMR, IR, and mass spectral data and/or analytical data are summarized below.

5-Norbornen-2-one. δ 1.7–2.3 (m, 4H), 2.9–3.0 (m, 1H), 3.1–3.3 (m, 1H), 6.0–6.3 (m, 1H), 6.4–6.7 (m, 1H); 1760, 1745, 1563 cm^{-1} (lit. [5] 1740, 1550 cm^{-1}); MS 108 (M^+).

1-Trimethylsilyl-2-hexanone. δ 0.10 (s, 9H), 0.8–1.0 (t, 3H), 1.1–1.7 (m, 4H), 2.05 (s, 2H), 2.24 (t, J 7 Hz, 2H); 1690 cm^{-1}; MS 172 (M^+, 4), 73 (100); Found: C, 63.02; H, 11.86. $C_9H_{20}OSi$ calcd.: C, 62.72; H, 11.70%.

Trimethylsilylmethyl phenyl ketone. (Not isolated pure; contaminated by acetophenone): δ 0.07 (s, 9H), 2.61 (s, 2H), 7.25–7.50 (m, 3H), 7.70–7.95 (m, 2H). 1660 cm^{-1}; MS 192 (M^+, 62), 177 (87), 83 (100); exact mass: Found: 192.0971. $C_{11}H_{16}OSi$ calcd.: 192.0971.

[(Trimethylsilyl)acetyl]trimethylsilane. b.p. ca. 110°C/40 Torr; 0.07 (s, 9H), 0.14 (s, 9H), 2.42 (s, 2H); 1620 cm^{-1}; MS 188 (M^+); exact mass: Found: 188.1077. $C_8H_{20}OSi_2$ calcd.: 188.1052.

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