

Correlation of Hydrolysis and Desilylation of 2-[(Trimethylsilyl)methyl]acrylate Derivatives in Aqueous Alkali Solutions

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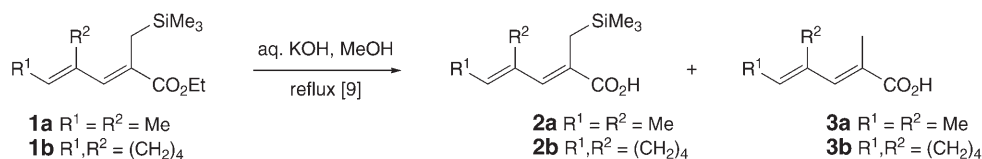
Hydrolysis and desilylation reaction of 2-[(trimethylsilyl)methyl]acrylate (=2-[(trimethylsilyl)methyl]prop-2-enoate) derivatives were studied to evaluate the effect of the presence/absence of a further conjugating substituent (*Schemes 3 and 4 and Tables 1 and 2*). The substrates having a nonconjugating substituent at the acrylate moiety were stable to dilute alkali conditions, and afforded simple hydrolysis products under concentrated alkali conditions. In contrast, both hydrolysis and desilylation occurred from the substrates bearing conjugated substituents at the acrylate skeleton. The difference in reactivity can be explained in terms of the stabilization of the intermediate anion.

Introduction. – The 2-[(trimethylsilyl)methyl]acrylate (=2-[(trimethylsilyl)methyl]prop-2-enoate) derivatives and their reduced forms, 2-[(trimethylsilyl)methyl]allyl alcohols (=2-[(trimethylsilyl)methyl]prop-2-en-1-ols), are versatile building blocks in organic synthesis [1]. These moieties act as C-1,3-dipole equivalent, because the allylsilane part is an allyl anion equivalent and the C=O group of the acrylate or the OH-bearing C-atom of the allyl alcohol is a cationic center. By means of these structural features, various synthetic reactions have been developed [2], including the ‘homo-Diels–Alder’ type [4+3] cycloaddition developed by *Hoffmann* and co-workers [3] and *Giguere* and co-workers [4]. We have reported the syntheses of some five-membered ring compounds such as γ -lactones [5], bicyclo[4.3.0]nonanes [6], and spiro[4.5]decanes [7], as well as cycloundecanes [8].

During the course of these projects, we previously obtained α -methylene- γ -lactones *via* a cyclization of 2-[(trimethylsilyl)methyl]pentadienoate or the corresponding carboxylic acid [9]. Moreover, ethyl (2*Z*,4*E*)-4-methyl-2-[(trimethylsilyl)methyl]hexa-2,4-dienoate (**1a**) and ethyl (2*Z*,4*E*)-3-(cyclohex-1-en-1-yl)-2-[(trimethylsilyl)methyl]hexa-2,4-dienoate (**1b**) were hydrolyzed to the corresponding acids **2a** and **2b** *via* a typical hydrolysis reaction, *i.e.*, in the presence of aqueous KOH solution in MeOH (*Scheme 1*). However, the yields of the hydrolysis products **2a** and **2b** were low (26% for **2a** and 31% for **2b**). Although not mentioned in the report, the major products were the desilylated acids **3a** and **3b**. Since direct desilylation from an allylsilane moiety does not occur under such weak-base conditions [10], the desilylation reaction proceeded presumably *via* an intramolecular assistance of the ester group or its hydrolyzed carboxylate. Indeed, intramolecular attack of an electron-rich anion or related species at the Si-atom as a *Lewis* base [11] is considered to facilitate protodesilylation. The aim of the present study is to clarify the generality and the substituent effect of this

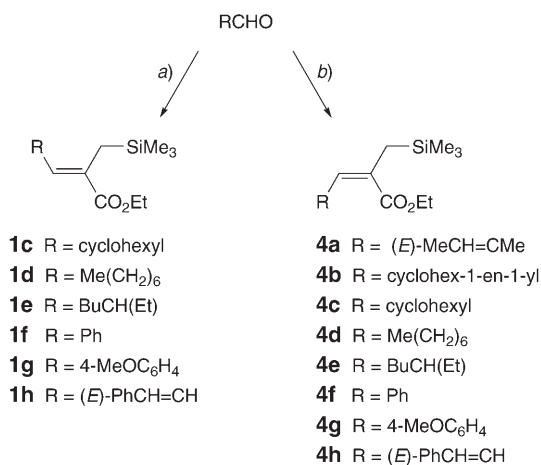
hydrolysis and desilylation process in the case of 2-[(trimethylsilyl)methyl]acrylate derivatives.

Scheme 1



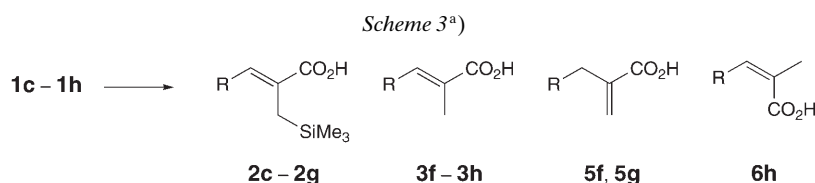
Results and Discussion. – To clarify the effect of conjugation and the geometry of the acrylate moiety, we chose both the conjugated and nonconjugated ethyl (*Z*)- and (*E*)-2-[(trimethylsilyl)methyl]acrylate derivatives **1c–h** and **4c–h** as the substrates of the present study. Compounds **1c–e** and **4c–e** have an aliphatic R group, and the C=C bond of the acrylate is not further conjugated, while compounds **1f–h** and **4f–h** bear an aromatic ring conjugated to the acrylate moiety. These compounds were synthesized from the corresponding aldehydes *via* a (*Z*)-selective [5a] and an (*E*)-selective [12] *Horner-Wadsworth-Emmons* (HWE) reaction, respectively (Scheme 2). Each of the substrates was obtained with good (*Z*)- or (*E*)-selectivity, except for **1c** and **1e** which were obtained with low (*Z*)-selectivity ((*E*)/(*Z*) 44:56 for **1c** and 22:78 for **1e**) when hexamethyldisilazane potassium salt (KHMDs)/[18]crown-6 was used as the base, while the standard method with NaH as the base [5a] afforded the (*E*)-product as the major isomer.

Scheme 2



a) For **1d,f,g,h**: (EtO)₂P(O)CH(CO₂Et)CH₂SiMe₃, NaH, THF, r.t.; for **1c,e**: (EtO)₂P(O)CH(CO₂Et)CH₂SiMe₃, KHMDs, [18]crown-6, THF, r.t. b) (PhO)₂P(O)CH(CO₂Et)CH₂SiMe₃, NaH, THF, r.t.

Subsequently, the hydrolysis/desilylation reaction was studied. The above substrates were treated with aqueous KOH solution in MeOH under reflux, as reported previously [9a], until the substrates disappeared on TLC. At first, the (*Z*)-isomers **1c–h** were treated, and the results are summarized in *Scheme 3* and *Table 1*. When **1c–e** were treated with 1M aqueous KOH in MeOH, the reaction was very slow, and a concentrated (30%) aqueous KOH solution was required to obtain the hydrolysis products **2c–e** in good yields (*Entries 1–3*). Furthermore, no desilylation products were detected. In contrast, desilylation occurred in the case of the aromatic substrates **1f–h** in 1M solution (*Entries 4–6*). Compounds **1f** and **1g** showed similar results to those reported for **1a** and **1b** (*Entries 4* and *5* vs. *Entries 7* and *8*), *i.e.*, **1f** and **1g** afforded the simple hydrolysis products **2f** and **2g** in low yield, while the desilylated compounds **3f** and **3g** were the major products, accompanied by the deconjugated products **5f** and **5g**. From substrate **1h**, mostly **3h** (90% yield) was formed, besides a small amount of the isomerization product **6h** (*Entry 6*).



^{a)} For R, see *Table 1*.

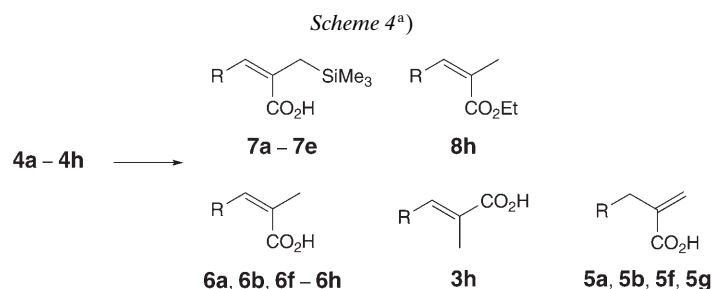
Table 1. Hydrolysis of Ethyl (*Z*)-2-[(Trimethylsilyl)methyl]acrylates **1a–h**^{a)}

Entry	Substrate	R	KOH (aq.)	Time	Product [%]			
					2	3	5	6
1	1c	cyclohexyl	30%	4.5 h	95	–	–	–
2	1d	Me(CH ₂) ₆	30%	7 h	94	–	–	–
3	1e	BuCH(Et)	30%	9 h	93	–	–	–
4	1f	Ph	1M	20 min	19	64	13	–
5	1g	4-MeOC ₆ H ₄	1M	20 min	30	54	9	–
6	1h	PhCH=CH	1M	1.5 h	–	90	–	2
7 ^{b)}	1a	MeCH=CMe	0.3M	8 h	26	^{c)}	–	–
8 ^{b)}	1b	cyclohex-1-en-1-yl	0.3M	8 h	31	^{c)}	–	–
9	1f	Ph	1M	3 h	–	87	12	–

^{a)} All reactions were carried out in boiling aq. KOH soln./MeOH 1 : 1 until no starting material could be detected on TLC. ^{b)} Results reported in [9a]. ^{c)} Major product. The yield had not been determined.

The results of the hydrolysis/desilylation reaction of the (*E*)-substrates **4c–h** are shown in *Scheme 4* and *Table 2*. In all cases, the reaction was slower than that of the corresponding (*Z*)-isomers, and more concentrated KOH solutions (for **4c–e**) or a longer reaction time was required. This is easily understood in view of the steric congestion caused by the substituent *cis* to the ester group. The results from the (*E*)-compounds **4c–e** were very similar to those of the (*Z*)-isomers, namely, the reaction proceeded only in concentrated alkali solutions giving the hydrolysis products **7c–e** in good yields (*Entries 1–3*). The desilylation products from **4f** and **4g** were obtained as

inseparable mixtures **5f/6f** and **5g/6g**, respectively, and their yields were calculated from the ratio observed in the $^1\text{H-NMR}$ spectra (*Entries 4* and *5*). Isomerization of the C=C bond occurred partly for the product from **4h** giving a mixture **3h/6h** (*Entry 6*); a noteworthy result is the formation of the simply desilylated ester **8h**, although its yield was only 2%.



^{a)} For R, see *Table 2*.

Table 2. Hydrolysis of Ethyl (E)-2-[(Trimethylsilyl)methyl]acrylates **4a–h**^{a)}

Entry	Substrate	R	KOH (aq.)	Time	Product [%]				
					7	6	3	5	8
1	4c	cyclohexyl	40%	4.5 h	99	–	–	–	–
2	4d	Me(CH ₂) ₆	40%	6 h	90	–	–	–	–
3	4e	BuCH(Et)	40%	2 h	95	–	–	–	–
4	4f	Ph	1M	3 h	–	50 ^{b)}	–	48 ^{b)}	–
5	4g	4-MeOC ₆ H ₄	1M	4 h	–	71 ^{b)}	–	26 ^{b)}	–
6	4h	PhCH=CH	1M	9 h	–	82	14	–	2
7	4a	MeCH=CMe	1M	7.5 h	8 ^{b)}	41	–	16 ^{b)}	–
8	4b	cyclohex-1-en-1-yl	1M	12 h	5 ^{b)}	34	–	15 ^{b)}	–

^{a)} All reactions were carried out in boiling aq. KOH soln./MeOH 1 : 1 until no starting material could be detected on TLC. ^{b)} The two products could not be separated. The yields were calculated based on the ratio of the products, obtained from the $^1\text{H-NMR}$ data of the product mixture.

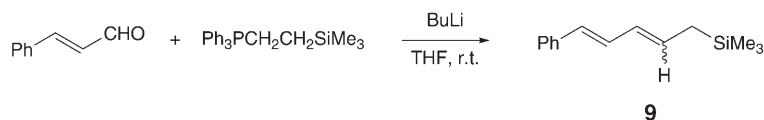
Compounds **4a** and **4b** were also prepared as substrates by the procedure shown in *Scheme 2*. When these compounds were treated under the hydrolysis conditions, several reaction products were detected on TLC, among which three major products, **5a** and **5b**, **6a** and **6b**, and **7a** and **7b**, respectively, were obtained after chromatography (*Table 2*, *Entries 7* and *8*). While the reaction products were complex, the results were roughly the same as in the case of the aromatic substrates.

Compound **2** (or **7**) was expected to be an intermediate formed from **1** to give **3** (or from **4** to give **6**). Thus, to clarify this, the effect of a longer reaction time was examined. When the reaction with **1f** was continued after the disappearance of the reactant, the amount of the simple hydrolysis product **2f** decreased, and only the desilylated products **3f** and **5f** were obtained after 3 h of refluxing (*Table 1*, *Entry 9*). Compound **2c** was similarly treated for a longer reaction time; however, no such further reaction

proceeded at all. These results indicate that **2f–h** and **7f–h** are the ‘intermediates’ on the way to the desilylated products, but **2c–e** and **7c–e** are the final products.

As a reference, treatment of allylsilane without an ester group was examined under the same reaction conditions. For this purpose, compound **9** [13] was prepared (*Scheme 5*; (*Z*)/(*E*) 78:22) and treated with aqueous KOH solution in MeOH; however, the product mixture was very complex even after reaction at room temperature. This result indicates that the desilylation reaction proceeds under participation of the ester group.

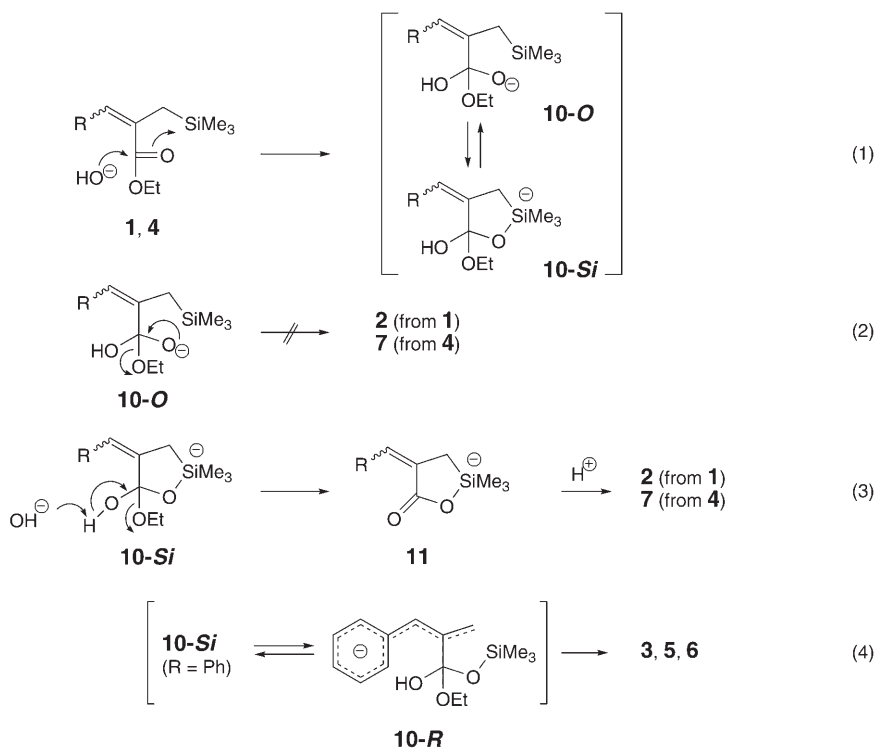
Scheme 5



From the above results, it is obvious that the reaction products depend on the substituent and partly on the geometry of the 2-[(trimethylsilyl)methyl]acrylate moiety. The results obtained from the present study are summarized by the following five observations: *i*) both the (*E*)- and (*Z*)-isomers of the substrates having a nonconjugated substituent, *i.e.*, **1c–e** and **4c–e**, were stable in dilute alkali solution; *ii*) these substrates afforded hydrolysis products in concentrated alkali solution in high yield without accompanying any desilylation products; *iii*) both hydrolysis and desilylation occurred at the same time from the substrates having a conjugated substituent, *i.e.*, from **1f–h** and **4f–h**, in dilute alkali; *iv*) the geometry of the C=C bond was mostly retained after the hydrolysis/desilylation reaction; however, isomerized products and deconjugated products were formed in small amounts; *v*) the reaction was faster for the (*Z*)-isomer than for the corresponding (*E*)-isomer, and only desilylated products were obtained from the (*E*)-isomer of the conjugated substrates **4f–h**, but simple hydrolysis products were also produced from the corresponding (*Z*)-isomers **1f** and **1g**.

These observations can be rationalized as follows. Since desilylation occurred from the hydrolysis product (*Table 1, Entry 9*), hydrolysis occurs prior to the desilylation as the major pathway, although the formation of **8h** (*Table 2, Entry 6*) implies that the desilylation pathway without hydrolysis is also present. The first step must be an attack of the hydroxide ion on the ester C=O group giving the anion **10-O**, which is stabilized by the Si-atom (**10-Si**), as predicted (*Scheme 6, Eqn. 1*). The above observation *i*) is justified by the stability of **10-Si**. Since both **1c–e** and **4c–e** did not afford the hydrolysis product in 1M solution within a ‘reasonable’ reaction time, the contribution of the normal hydrolysis pathway (*Eqn. 2*) must be small. In concentrated solution, further deprotonation of **10-Si** occurred to give **11** (*Eqn. 3*) from which the hydrolysis product is considered to be generated. For the aromatic substrates **1f–h** and **4f–h**, the above observation *iii*) implies that the desilylation reaction is assisted by a ‘further-conjugated’ aromatic ring. We presume that the cleavage of the C–Si bond is promoted by the contribution of the highly conjugated anion **10-R** (*Eqn. 4*). This also explains the fact that (*E*)/(*Z*) isomerization occurred in only limited amounts (observation *iv*)).

Scheme 6



In conclusion, it was found that the two reactions, hydrolysis and desilylation, of 2-[(trimethylsilyl)methyl]acrylate derivatives in aqueous KOH solution are not independent but correlated. The desilylation is considered to be assisted by the ester group, and the hydrolysis was affected by the Si-atom. These reactions occurred in aqueous media, in which organosilicon compounds act as a H₂O-stable carbanion equivalent. We hope that the present results provide useful information for the study of organic reactions in H₂O, which are currently extensively developed [14].

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Experimental Part

General. Anhydrous Na₂SO₄ or MgSO₄ was used for drying the extracted organic layers. Anal. TLC: precoated TLC plates (silica gel 60 F254, layer thickness 0.2 mm). Column chromatography (CC): Wakogel C-200 or Florisil (100–200 mesh). M.p.: Laboratory-Devices-Mel-Temp apparatus. IR Spectra: Jasco-FT/IR-230 spectrometer, $\tilde{\nu}$ in cm⁻¹. ¹H- and ¹³C-NMR Spectra: Jeol-GSX-400 (400 MHz for ¹H; 100 MHz for ¹³C) spectrometer; CDCl₃; δ in ppm with residual solvent (δ (CHCl₃) 7.26; δ (CDCl₃) 77.0) as internal standard, *J* in Hz. EI-MS and HR-EI-MS: Jeol-SX-102A, CMATE-II, or Shimadzu-GCMS-QP5050 apparatus; in *m/z* (rel. %).

Substrates 1c–h by the (Z)-Selective HWE Reaction. The procedure by which **1g** (96% yield) and **1h** (97% yield) were synthesized from 4-methoxybenzaldehyde and cinnamaldehyde (= (2E)-3-phenylprop-2-enal), resp., has been reported in our previous paper [5a].

Ethyl (2Z)-3-(4-Methoxyphenyl)-2-[(trimethylsilyl)methyl]prop-2-enoate (1g): Oil. IR (neat): 2954, 1705, 1512, 1252, 845. ¹H-NMR: 0.01 (s, Me₃Si); 1.34 (t, *J* = 7.2, MeCH₂O); 2.20 (br. s, Me₃SiCH₂); 3.83 (s, MeO); 4.25 (q, *J* = 7.2, MeCH₂O); 6.88–6.92 (m, 2 arom. H); 7.35–7.39 (m, 2 arom. H); 7.50 (s, CH=CCO₂Et). ¹³C-NMR: –0.8 (3 C); 14.3; 17.6; 55.2; 60.7; 113.7 (2 C); 129.1; 129.6; 130.8 (2 C); 134.5; 159.2; 169.2. EI-MS: 292 (5, *M*⁺), 277 (6), 249 (4), 202 (7), 173 (10), 146 (21), 73 (100). HR-EI-MS: 292.1504 (*M*⁺, C₁₆H₂₄O₃Si⁺; calc. 292.1495).

Ethyl (2Z,4E)-5-Phenyl-2-[(trimethylsilyl)methyl]penta-2,4-dienoate (1h): Oil. IR (neat): 2954, 1701, 1288, 852. ¹H-NMR: 0.04 (s, Me₃Si); 1.33 (t, *J* = 7.0, MeCH₂O); 2.07 (br. s, Me₃SiCH₂); 4.23 (q, *J* = 7.0, MeCH₂O); 6.81 (d, *J* = 15.3, PhCH=CH); 6.95 (dd, *J* = 11.2, 15.3, PhCH=CH); 7.25–7.47 (m, 5 arom. H, CH=CCO₂Et). ¹³C-NMR: –1.1 (3 C); 14.3; 18.2; 60.6; 124.8; 126.8 (2 C); 128.3; 128.8 (2 C); 130.7; 134.6; 137.0; 137.3; 168.4. EI-MS: 288 (4, *M*⁺), 243 (2), 170 (17), 141 (38), 73 (100). HR-EI-MS: 289.1608 ([*M* + H]⁺, C₁₇H₂₅O₂Si⁺; calc. 289.1624).

Spectroscopic data of **1c–f** [15] have already been reported.

Substrates 4a–h by the (E)-Selective HWE Reaction. The procedure by which **4g** (94% yield) was synthesized from 4-methoxybenzaldehyde has been reported in our previous paper [12].

Ethyl (2E)-3-(4-Methoxyphenyl)-2-[(trimethylsilyl)methyl]prop-2-enoate (4g): Oil. IR (neat): 2954, 1712, 1510, 1252, 856. ¹H-NMR: –0.09 (s, Me₃Si); 1.15 (t, *J* = 7.2, MeCH₂O); 1.89 (br. s, Me₃SiCH₂); 3.79 (s, MeO); 4.11 (q, *J* = 7.2, MeCH₂O); 6.43 (s, CH=CCO₂Et); 6.79–6.83 (m, 2 arom. H); 7.14–7.19 (m, 2 arom. H). ¹³C-NMR: –1.6 (3 C); 13.8; 25.7; 55.1; 60.3; 113.3 (2 C); 129.3; 129.4 (2 C); 130.8; 130.9; 158.7; 170.2. EI-MS: 292 (6, *M*⁺), 277 (5), 249 (4), 202 (7), 173 (9), 146 (25), 73 (100). HR-EI-MS: 292.1546 (*M*⁺, C₁₆H₂₄O₃Si⁺; calc. 292.1495).

Spectroscopic data of **4a** and **4b** [9a] and of **4c–f** and **4h** [12] have already been reported.

Typical Procedure of the Hydrolysis and Desilylation Reaction. A soln. of 1M aq. KOH (5.0 ml) was added to a stirred soln. of **4f** (144.0 mg, 0.549 mmol) in MeOH (5 ml), and the mixture was refluxed for 3 h. After cooling to r.t., 2M aq. HCl (ca. 5 ml) was added until the soln. became acidic. Extraction with AcOEt followed by drying and evaporation of the solvent afforded an oily residue, which was subjected to CC (SiO₂ (13 g), hexane/AcOEt 95 : 5 → 75 : 25): **5f** (44.0 mg, 50%) and **6f** (42.3 mg, 48%).

For the hydrolysis of **1c–e** and **4c–e**, conc. aq. KOH was used instead of 1M soln.; see text. All the hydrolysis results are provided in *Tables 1* and *2*.

(2Z)-3-Cyclohexyl-2-[(trimethylsilyl)methyl]prop-2-enoic Acid (2c): M.p. 99–101°. IR (KBr): 2300–3300 (br.), 2927, 1672, 1304, 845. ¹H-NMR: 0.03 (s, Me₃Si); 1.09–1.35 (m, 5 H); 1.60–1.82 (m, 5 H); 1.80 (br. s, Me₃SiCH₂); 2.21 (tq, *J* = 3.4, 10.5, CHC=C); 6.60 (d, *J* = 10.0, CH=C). ¹³C-NMR: –1.2 (3 C); 16.7; 25.6 (2 C); 25.9; 31.8 (2 C); 38.2; 127.4; 146.1; 174.5. EI-MS: 240 (5, *M*⁺), 225 (14), 209 (4), 143 (23), 121 (30), 73 (100). HR-EI-MS: 240.1549 (*M*⁺, C₁₃H₂₄O₂Si⁺; calc. 240.1546).

(2E)-3-Cyclohexyl-2-[(trimethylsilyl)methyl]prop-2-enoic Acid (7c): M.p. 99–100°. IR (KBr): 2300–3400 (br.), 2927, 1678, 1248, 843. ¹H-NMR: 0.00 (s, Me₃Si); 0.96–1.23 (m, 5 H); 1.62–1.76 (m, 5 H); 1.72 (br. s, Me₃SiCH₂); 2.98 (tq, *J* = 3.3, 10.5, CHC=C); 5.63 (d, *J* = 9.8, CH=C). ¹³C-NMR: –1.8 (3 C); 23.7; 25.6 (2 C); 26.0; 33.1 (2 C); 38.2; 126.3; 147.8; 174.2. EI-MS: 240 (3, *M*⁺), 225 (7), 209 (3), 143 (19), 121 (30), 73 (100). HR-EI-MS: 240.1529 (*M*⁺, C₁₃H₂₄O₂Si⁺; calc. 240.1546).

(2Z)-2-[(Trimethylsilyl)methyl]dec-2-enoic Acid (2d): Oil. IR (neat): 2300–3400 (br.), 2929, 1680, 1421, 1286, 856. ¹H-NMR: –0.02 (s, Me₃Si); 0.85 (*t*-like, *J* = 6.7, Me); 1.19–1.44 (m, 10 H); 1.76 (br. s, Me₃SiCH₂); 2.08 (q, *J* = 7.3, CH₂C=C); 6.73 (t, *J* = 7.3, CH=C). ¹³C-NMR: –1.1 (3 C); 14.1; 16.9; 22.6; 28.7; 29.1; 29.3; 29.4; 31.8; 129.3; 141.5; 174.0. EI-MS: 256 (1, *M*⁺), 241 (16), 169 (19), 95 (37), 73 (100). HR-EI-MS: 256.1783 (*M*⁺, C₁₄H₂₈O₂Si⁺; calc. 256.1859).

(2E)-2-[(Trimethylsilyl)methyl]dec-2-enoic Acid (7d): Oil. IR (neat): 2300–3400 (br.), 2927, 1687, 1425, 1248, 847. ¹H-NMR: 0.02 (s, Me₃Si); 0.89 (*t*-like, *J* = 6.8, Me); 1.25–1.46 (m, 10 H); 1.76 (br. s, Me₃SiCH₂); 2.50 (q, *J* = 7.3, CH₂C=C); 5.85 (t, *J* = 7.5, CH=C). ¹³C-NMR: –1.7 (3 C); 14.1; 22.7; 23.7; 29.1; 29.3; 29.8; 29.9; 31.8; 128.3; 143.1; 174.4. EI-MS: 241 (9, [*M* – Me]⁺), 169 (20), 95 (37), 73 (100). HR-EI-MS: 256.1825 (*M*⁺, C₁₄H₂₈O₂Si⁺; calc. 256.1859).

(2*Z*)-4-Ethyl-2-[(trimethylsilyl)methyl]oct-2-enoic Acid (**2e**): Oil. IR (neat): 2400–3400 (br.), 2958, 1684, 1290, 1250, 852. ¹H-NMR: 0.04 (s, Me₃Si); 0.88 (t, *J* = 7.4, Me); 0.89 (t-like, *J* = 6.8, Me); 1.22–1.55 (m, 8 H); 1.80 (br. s, Me₃SiCH₂); 2.17–2.27 (m, CHC=C); 6.57 (d, *J* = 10.2, CH=C). ¹³C-NMR: –0.8 (3 C); 11.7; 14.0; 17.0; 23.1; 27.5; 29.5; 34.2; 40.3; 129.1; 146.3; 174.5. EI-MS: 241 (10, [*M* – Me]⁺), 211 (3), 197 (3), 183 (5), 169 (7), 109 (38), 73 (100). HR-EI-MS: 256.1802 (*M*⁺, C₁₄H₂₈O₂Si⁺; calc. 256.1859).

(2*E*)-4-Ethyl-2-[(trimethylsilyl)methyl]oct-2-enoic Acid (**7e**): Oil. IR (neat): 2400–3400 (br.), 2958, 1687, 1248, 850. ¹H-NMR: 0.02 (s, Me₃Si); 0.86 (t, *J* = 7.3, Me); 0.87 (t-like, *J* = 6.9, Me); 1.13–1.52 (m, 8 H); 1.78 (br. s, Me₃SiCH₂); 2.99–3.10 (m, CHC=C); 5.55 (d, *J* = 10.3, CH=C). ¹³C-NMR: –1.6 (3 C); 11.7; 14.1; 22.9; 24.1; 28.6; 29.6; 35.2; 40.4; 128.4; 147.3; 174.5. EI-MS: 241 (5, [*M* – Me]⁺), 211 (4), 197 (4), 183 (5), 169 (6), 109 (34), 73 (100). HR-EI-MS: 256.1798 (*M*⁺, C₁₄H₂₈O₂Si⁺; calc. 256.1859).

(2*Z*)-3-Phenyl-2-[(trimethylsilyl)methyl]prop-2-enoic Acid (**2f**): Oil. IR (neat): 2400–3500 (br.), 1682, 1250, 841. ¹H-NMR: 0.03 (s, Me₃Si); 2.22 (s, Me₃SiCH₂); 7.29–7.45 (m, Ph); 7.70 (s, CH=C). ¹³C-NMR: –0.8 (3 C); 17.6; 128.2; 128.4 (2 C); 129.3 (2 C); 130.8; 136.3; 137.0; 174.4. EI-MS: 234 (1, *M*⁺), 219 (16), 144 (20), 116 (100), 73 (81). HR-EI-MS: 234.1095 (*M*⁺, C₁₃H₁₈O₂Si⁺; calc. 234.1076).

The structure of **5f** [16] was determined based on literature. Compounds **3f** and **6f** are commercially available.

(2*Z*)-3-(4-Methoxyphenyl)-2-[(trimethylsilyl)methyl]prop-2-enoic Acid (**2g**): Oil. IR (neat): 2300–3400 (br.), 1660, 1603, 1259, 1178, 831. ¹H-NMR: 0.04 (s, Me₃Si); 2.22 (br. s, Me₃SiCH₂); 3.48 (s, MeO); 6.90–6.94 (m, 2 arom. H); 7.40–7.44 (m, 2 arom. H); 7.64 (s, CH=CCO₂H). ¹³C-NMR: –0.8 (3 C); 17.6; 55.3; 113.9 (2 C); 128.4; 128.8; 131.2 (2 C); 136.7; 159.6; 174.2. EI-MS: 249 (13, [*M* – Me]⁺), 175 (12), 146 (100), 73 (72), 45 (83). HR-EI-MS: 264.1226 (*M*⁺, C₁₄H₂₀O₃Si⁺; calc. 264.1182).

The structures of **3g** [17], **5g** [18], and **6g** [16], and of **3h** [19], **6h** [19], and **8h** [20] were determined based on the literature.

(2*Z*,4*E*)-2,4-Dimethylhexa-2,4-dienoic Acid (**6a**): Oil. IR (CHCl₃): 1691, 1454, 1261, 1138. ¹H-NMR: 1.69 (d, *J* = 6.8, Me–C(5)); 1.77 (s, Me–C(4)); 1.99 (d, *J* = 0.8, Me–C(2)); 5.61 (q, *J* = 6.8, MeCH=C); 6.28 (br. s, CH=CCO₂H). ¹³C-NMR: 13.9; 14.8; 21.3; 124.8; 128.8; 133.2; 140.8; 175.7. EI-MS: 140 (21, *M*⁺), 125 (100), 79 (39). HR-EI-MS: 140.0838 (*M*⁺, C₈H₁₂O₂⁺; calc. 140.0837).

(4*E*)-4-Methyl-2-methylenehex-4-enoic Acid (**5a**) and (2*E*,4*E*)-4-Methyl-2-[(trimethylsilyl)methyl]hexa-2,4-dienoic Acid (**7a**): The individual compounds could not be isolated in pure form. The following spectral data were obtained from a mixture. IR (neat): 2400–3400 (br.), 1695, 1629, 1249, 856. ¹H-NMR: **5a**: 1.59 (s, Me–C(4)); 1.61 (br. d, *J* = 7, Me–C(5)); 2.97 (s, C=CCH₂C=C); 5.26–5.33 (m, MeCH=C); 5.62 (q, *J* = 1.3, 1 H, C=CH₂); 6.34 (dt, *J* = 1.3, 0.7, 1 H, C=CH₂); **7a**: 0.05 (s, Me₃Si); 1.68 (d, *J* = 6.8, Me–C(5)); 1.76 (br. s, Me–C(4)); 1.77 (s, Me₃SiCH₂); 5.56 (q, ‘quint.’, *J* = 6.8, 1.2, MeCH=C); 6.07 (br. s, CH=CCO₂H). ¹³C-NMR: **5a**: 13.5; 15.6; 40.7; 121.5; 127.9; 132.4; 138.4; 172.4; **7a**: –1.6 (3 C); 14.0; 15.1; 25.1; 127.4; 127.5; 133.5; 137.9; 174.6. GC/MS: **5a**: 140 (8, *M*⁺), 125 (25, [*M* – Me]⁺), 111 (13), 79 (32), 40 (100); **7a**: 197 (4, [*M* – Me]⁺), 122 (25), 107 (22), 73 (100). HR-EI-MS: **5a**: 140.0846 (*M*⁺, C₈H₁₂O₂⁺; calc. 140.0837); **7a**: 212.1226 (*M*⁺, C₁₁H₂₀O₂Si⁺; calc. 212.1233).

(2*Z*)-3-(Cyclohex-1-en-1-yl)-2-methylprop-2-enoic Acid (**6b**): Oil. IR (neat): 2400–3400 (br.), 1690, 1455, 1256, 1190, 927. ¹H-NMR: 1.55–1.65 (m, 4 H); 1.99 (d, *J* = 0.8, Me); 2.09–2.18 (m, 4 H); 5.77–5.81 (m, CH=C in ring); 6.20 (br. s, CH=CCO₂H). ¹³C-NMR: 21.4; 21.8; 22.6; 25.9; 26.8; 124.5; 131.3; 134.9; 139.6; 175.5. EI-MS: 166 (27, *M*⁺), 121 (48), 79 (70), 41 (100). HR-EI-MS: 166.0996 (*M*⁺, C₁₀H₁₄O₂⁺; calc. 166.0994).

2-(Cyclohex-1-en-1-yl)methylprop-2-enoic Acid (**5b**) and (2*E*)-3-(Cyclohex-1-en-1-yl)-2-[(trimethylsilyl)methyl]prop-2-enoic Acid (**7b**): The individual compound could not be isolated in pure form. The following spectral data were obtained from a mixture. IR (neat): 2400–3400 (br.), 1693, 1626, 1438, 1248, 851. ¹H-NMR: **5b**: 1.51–1.65 (m, 4 H); 1.88–1.94 (m, 2 H); 1.97–2.04 (m, 2 H); 2.92 (br. s, C=CCH₂C=C); 5.45–5.49 (m, CH=C in ring); 5.63 (q, *J* = 1.2, 1 H, C=CH₂); 6.33 (d, *J* = 1.2, 1 H, C=CH₂); **7b**: 0.04 (s, Me₃Si); 1.51–1.65 (m, 4 H); 1.77 (s, Me₃SiCH₂); 2.08–2.15 (m, 4 H); 5.70–7.74 (m, CH=C in ring); 5.98 (br. s, CH=CCO₂H). ¹³C-NMR: **5b**: 22.3; 22.9; 25.3; 28.1; 39.2; 123.8; 127.9; 134.6; 138.3; 172.8; **7b**: –1.6 (3 C); 21.9; 22.7; 25.3; 25.9; 27.1; 127.4; 129.9; 135.3; 136.5; 175.7. GC/MS: **5b**: 166 (9, *M*⁺), 123 (10), 91 (18), 81 (100), 41 (61); **7b**: 238 (1, *M*⁺), 223 (2, [*M* – Me]⁺), 148 (19), 120 (21), 105

(19), 91 (33), 73 (100). HR-EI-MS: **5b**: 166.0971 (M^+ , $C_{10}H_{14}O_2^+$; calc. 166.0994); **7b**: 238.1375 (M^+ , $C_{13}H_{22}O_2Si^+$; calc. 238.1389).

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