COMMUNICATIONS

- New or improved synthetic methods
- Key intermediates
- with full experimental and analytical data

3-Metallated Enamines; VII[1]. 3-Oxosilanes via Silylation of 3-Metallated Enamines

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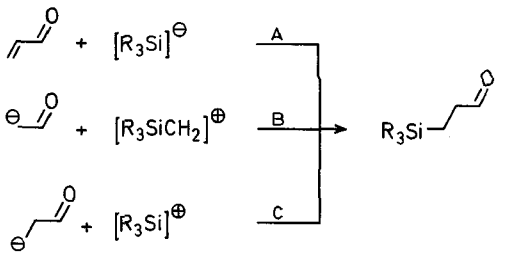
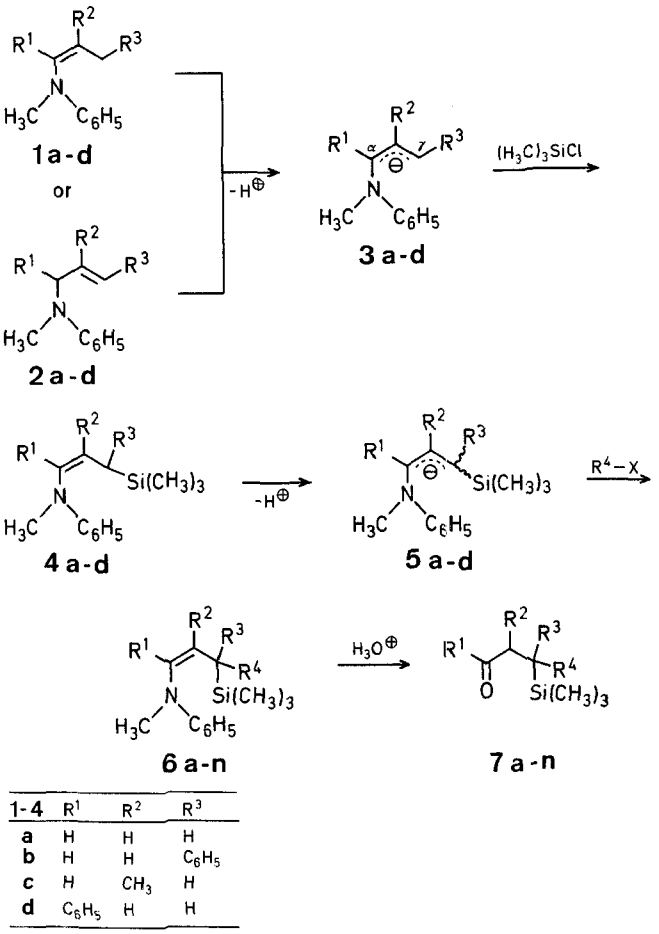
3-Oxosilanes have been the subject of increasing interest recently since they can be used as protected α,β-unsaturated carbonyl compounds[3,4]. They are normally prepared from carbonyl compounds using the routes A or B, that is 1,4-addition of a nucleophilic silicon to an α,β-unsaturated carbonyl compound[4,5,6] or alkylation of an enolate with a silylated methyl halide[3,7].



A third possibility, C, that is silylation of an homoenolate with a halosilane has been used only rarely[8].

As we have shown recently[9], enamines **1** or allylamines **2** can be deprotonated to give ambident 1-aminoallyl anions **3**, useful homoenolate equivalents. Reaction of **3** with chlorotrimethylsilane occurs with high regioselectivity at the γ-position to yield the silylated enamines **4** only. The latter products can be hydrolysed without loss of silicon by dilute hydrochloric acid to give 3-oxosilanes of the type **7** ($R^4 = H$, see entries **e** and **j** in Table 1). Hence, the site of protonation of **4** is completely controlled by nitrogen, not by silicon.

The versatility of this 3-oxosilane synthesis is broadened remarkably by the possibility of a further deprotonation of **4** to



1-4	R^1	R^2	R^3
a	H	H	H
b	H	H	C_6H_5
c	H	CH_3	H
d	C_6H_5	H	H

Table 1. Preparation of 3-Oxosilanes **7**

Product	R^1	R^2	R^3	R^4X	Yield [%]	b.p. [°C]/ torr[a]	Molecular formula[b]	Metallation (Alkylation) conditions Method/time [h]
7a	H	H	H	C_2H_5J	76	62°/13	$C_8H_{18}OSi$ (158.3)	A/8 (1)
7b	H	H	H	*c*-C_5H_9Br	61	65°/1	$C_{11}H_{22}OSi$ (198.4)	A/8 (3)
7c	H	H	H	*n*-$C_6H_{13}Br$	75	70°/1	$C_{12}H_{26}OSi$ (214.4)	A/8 (5)
7d	H	H	H	*n*-$C_8H_{17}Br$	78	80°/1	$C_{14}H_{30}OSi$ (242.5)	A/8 (2)
7e	H	H	C_6H_5	H—	71	50°/1	$C_{12}H_{18}OSi$ (206.4)	—/—
7f	H	H	C_6H_5	C_2H_5J	70	85°/1	$C_{14}H_{22}OSi$ (234.4)	A/6.5 (1)
7g	H	CH_3	H	*n*-$C_5H_{11}Br$	89	80°/1	$C_{12}H_{26}OSi$ (214.4)	B/4 (1.5)
7h	H	CH_3	H	*n*-$C_6H_{13}Br$	75	85°/1	$C_{13}H_{28}OSi$ (228.5)	B/4 (1.5)
7i	H	CH_3	H	*n*-$C_8H_{17}Br$	77	90°/1	$C_{15}H_{32}OSi$ (256.5)	B/4 (1.5)
7j	C_6H_5	H	H	H—	73	65°/1	$C_{12}H_{18}OSi$ (206.4)	—/—
7k	C_6H_5	H	H	CH_3J	73	80°/1	$C_{13}H_{20}OSi$ (220.4)	A/3 (1)
7l	C_6H_5	H	H	C_2H_5J	85	85°/1	$C_{14}H_{22}OSi$ (234.4)	A/3 (1)
7m	C_6H_5	H	H	*i*-C_3H_7J	76	85°/1	$C_{15}H_{24}OSi$ (248.4)	A/3 (2.5)
7n	C_6H_5	H	H	C_3H_5Br	78	95°/1	$C_{15}H_{22}OSi$ (246.4)	A/3 (1)

[a] Temperature of kugelrohr oven, about 20 °C above b.p.

[b] The microanalyses were in satisfactory agreement with the calculated values: C ±0.30, H ±0.20; Exceptions: **7a** (C +0.86); **7e** (C −0.63).

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give **5** and subsequent alkylation to give **6**. The enamines **6** can be isolated or hydrolysed without further purification to the homologous 3-oxosilanes **7** in good overall yield (Table 1).

There are two remarkable points to be noticed in this sequence. Firstly, during distillation of **4**, partial or complete (*Z*)→(*E*)-isomerisation occurs. Owing to the activating effect of silicon, this has no influence on the subsequent deprotonation, in contrast to the case with other enamines where the (*Z*)-configuration is normally essential for deprotonation[9]. The enamines **6**, before distillation, have again the (*Z*)-configuration. Hence, during deprotonation reaction, isomerisation of the less stable *exo*- to the more stable *endo*-1-aminoallyl anion must have been occurred as expected[9]. Secondly, in addition to the fact that the presence of the bulky silyl group introduces considerable steric hindrance, alkylation even with secondary alkyl halides (see entries **b** and **m** in Table 1) occurs in

Table 2. Spectroscopic Data for 3-Oxosilanes **7**

Product	I.R.[a] ν [cm^{-1}]	^{1}H-N.M.R.[b] δ [ppm], J [Hz]	^{13}C-N.M.R.[c] δ [ppm]
7a	2960, 2920, 2900, 2870, 1720, 1255, 1245, 835, 745, 685	−0.08 [s, Si(CH$_3$)$_3$]; 0.76 (t, J=7, CH$_3$); 0.8–1.6 (m, CHSi, CH$_2$CH$_3$); 1.9–2.1 (m, CH$_2$CO); 9.38 (t, J=2.5, CHO)	−2.5 [q, Si(CH$_3$)$_3$]; 13.9 (q, CH$_3$); 21.9 (d, CH—Si); 23.3 [t, CH$_2$CH$_3$]; 44.3 (t, CH$_2$CO); 201.2 (d, CHO)
7b	2950, 2910, 2870, 1720, 1245, 855, 835	−0.02 [s, Si(CH$_3$)$_3$]; 0.71–1.8 (m, broad, aliphatic CH); 2.08 (dd, J=5.5, 1.8, CH$_2$CO); 9.38 (t, J=1.8, CHO)	−1.4 [q, Si(CH$_3$)$_3$]; 24.6, 25.0, 25.4, 32.1, 33.1, 41.9, 43.6 (CH, CH$_2$); 201.5 (d, CHO)
7c	2950, 2920, 2850, 1720, 1245, 850, 825, 745, 680	−0.08 [s, Si(CH$_3$)$_3$]; 0.87 (t, CH$_3$); 1.19 (s, broad, CH$_2$, CHSi); 1.96 (d, broad, CH$_2$CO); 9.36 (t, J=1.9, CHO)	−2.5 [q, Si(CH$_3$)$_3$]; 14.2 (q, CH$_3$); 20.0 (d, CH—Ci); 23.0 (t, CH$_2$CHSi); 29.5, 29.8, 30.7, 32.1 (CH$_2$); 44.8 (t, CH$_2$CO); 201.0 (d, CHO)
7d	2950, 2920, 2850, 1725, 1245, 850, 835, 745, 685	−0.07 [s, Si(CH$_3$)$_3$]; 0.74 (t, broad, CH$_3$); 1.1 (s, broad, CH$_2$); 1.92 (d, broad, CH$_2$CO); 9.48 (t, J=2, CHO)	−2.6 [q, Si(CH$_3$)$_3$]; 14.3 (q, CH$_3$); 19.8 (d, CHSi); 23.0 (t, CH$_2$CHSi); 29.5, 29.7, 29.9, 30.1, 30.6, 32.2 (CH$_2$); 44.7 (t, CH$_2$CO); 201.0 (d, CHO)
7e	2980, 1725, 1250, 855, 835, 695	−0.12 [s, Si(CH$_3$)$_3$]; 2.3–3.0 (m, CH$_2$, CHSi); 7.3–7.8 (m, C$_6$H$_5$); 9.5 (s, broad, CHO)	−3.2 [q, Si(CH$_3$)$_3$]; 30.2 (d, CHSi); 43.5 (t, CH$_2$CO); 125.1 (d, *p*-C); 127.7, 128.5 (d, *m*-C + *o*-C); 200.7 (d, CHO)
7f	2960, 2930, 1720, 1250, 860, 835, 750, 700	−0.16 [s, Si(CH$_3$)$_3$]; 0.77 (t, J=7, CH$_3$); 1.9 (centre of m, CH$_2$CH$_3$); 2.66 (d+AB q, J=2.8, 16); 9.53 (t, J=2.8, CHO)	−2.7 [Si(CH$_3$)$_3$]; 10.0 (CH$_3$); 26.7 (CH$_2$); 34.9 (CSi); 46.8 (CH$_2$CO); 125.4 (*p*-C); 127.5, 128.9 (*m*-C + *o*-C); 203.4 (CHO)
7g[d]	2970, 2935, 2865, 2810, 1720, 1455, 1250, 835, 745, 685	−0.04, −0.01 [2s, (SiCH$_3$)$_3$]; 0.7–1.0 (m); 1.15 (s, broad); 1.8–2.4 (m, CH—CO); 9.44 (s, CHO)	−1.3, −0.7 [q, Si(CH$_3$)$_3$]; 10.5, 12.5 (d, CHSi); 14.2 (q, CH$_2$CH$_3$); 22.9 (t, CH$_2$); 26.3, 26.6, 27.7, 28.3, 29.3, 30.4, 32.2, 32.4[e], 47.2, 47.9 (d, CHCO); 203.8, 204 (d, CHO)
7h[d]	2960, 2930, 2850, 1725, 1690, 1250, 850, 835, 750, 685	−0.04 [s, Si(CH$_3$)$_3$]; 0.7–1.1 (m); 1.24 (s, broad); 1.9–2.3 (m, CH—CO); 9.35 (s, CHO)	−1.3, −0.7 [q, Si(CH$_3$)$_3$]; 10.4, 12.4 (d, CHSi); 14.4 (q, CH$_2$CH$_3$); 23.1 (t, CH$_2$); 26.1, 26.7, 27.6, 28.3, 29.5, 29.7, 29.8, 30.0, 30.7, 31.1[e]; 47.2, 47.8 (d, CHCO); 203.9, 204.2 (d, CHO)
7i[d]	2960, 2930, 2850, 1725, 1250, 850, 835	0.03 [s, Si(CH$_3$)$_3$]; 0.6–1.05 (m); 1.27 (s, broad); 1.85–2.5 (m, CHCO); 9.5 (s, CHO)	−1.3, −0.7 [q, Si(CH$_3$)$_3$]; 10.5, 12.5 (d, CHSi); 14.3 (q, CH$_2$CH$_3$); 23.1 (t, CH$_2$); 26.3, 26.7, 27.7, 28.4, 29.7, 30.1, 30.8, 32.3[e]; 47.2, 47.9 (d, CHCO); 203.8, 204.0 (d, CHO)
7j	2950, 2900, 1690, 1600, 1450, 1250, 1230, 965, 860, 840, 745, 690	0.09 [s, Si(CH$_3$)$_3$]; 0.93 (m, CH$_2$Si); 2.96 (m, CH$_2$CO); 7.3–7.8, 8–8.2 (2m, C$_6$H$_5$)	−1.7 [q, Si(CH$_3$)$_3$]; 10.9 (t, CH$_2$Si); 33.0 (t, CH$_2$CO); 128.0, 128.5 (d, *o*-C + *m*-C); 132.6 (d, *p*-C); 137.0 (s, *i*-C); 200.6 (s, CO)
7k	2960, 2910, 2880, 1690, 1600, 1450, 1250, 1230, 860, 840, 750, 690	0.04 [s, Si(CH$_3$)$_3$]; 0.94 (d, J=7, CH$_3$); 1.16–1.48 (m, CHSi); 2.62 (dd, J=16, 9.8) and 2.96 (dd, J=16, 4.8, diastereotopic CH$_2$); 7.3–7.6, 7.8–8.1 (2m, C$_6$H$_5$)	−3.3 [q, Si(CH$_3$)$_3$]; 14.6 (q, CH$_3$); 16.1 (d, CHSi); 40.8 (t, CH$_2$); 128.0, 128.5 (d, *o*-C + *m*-C); 132.6 (d, *p*-C); 137.4 (s, *i*-C); 200.1 (s, CO)
7l	2960, 2900, 2875, 1690, 1600, 1450, 1250, 1225, 1210, 860, 835, 795, 690	0.07 [s, Si(CH$_3$)$_3$]; 0.89 (t, J=7, CH$_3$); 1.15–1.7 (m, CH, CH$_2$CH$_3$); 2.93 (centre of m, CH$_2$CO); 7.3–7.7, 7.9–8.1 (2m, C$_6$H$_5$)	−2.3 [q, Si(CH$_3$)$_3$]; 13.8 (q, CH$_3$); 23.1 (d, CHSi); 23.4 (t, CH$_2$CH$_3$); 38.7 (t, CH$_2$CO); 128.0, 128.5 (d, *o*-C + *m*-C); 132.6 (d, *p*-C); 137.5 (s, *i*-C); 200.0 (s, CO)
7m	2970, 2900, 2880, 1690, 1600, 1450, 1255, 1230, 1215, 860, 835, 750, 690	0.05 [s, Si(CH$_3$)$_3$]; 0.88, 0.92 (d, J=7) diastereotopic CH$_3$); 1.5–1.7 (m, CHSi); 1.8–2.2 (m, CHC); 3.01 (centre of AB-part of ABX m, J_{AB}=17, CH$_2$CO); 7.2–7.5, 7.7–7.9 (2m, C$_6$H$_5$)	−0.9 [q, Si(CH$_3$)]; 21.4, 22.8 (q, diastereotopic CH$_3$); 28.3, 29.0 (d, CH); 36.0 (t, CH$_2$CO); 128.1, 128.6 (d, *o*-C + *m*-C); 132.7 (d, *p*-C); 137.4 (s, *i*-C); 201.0 (s, CO)
7n	2960, 2900, 1690, 1600, 1450, 1255, 1220, 995, 915, 855, 835, 750, 690	0.04 [s, Si(CH$_3$)$_3$]; 1.3–1.7 (m, CHSi); 1.8–2.4 (m, CH$_2$CH=); 2.91 (d, J=6.8, CH$_2$CO); 4.75–5.04 (m, C=CH$_2$); 5.5–5.9 (m, CH=C); 7.2–7.6, 7.8–8.0 (2m, C$_6$H$_5$)	−2.3 [q, Si(CH$_3$)$_3$]; 20.7 (d, CH); 34.8 (t, CH$_2$CH=); 38.3 (t, CH$_2$CO); 115.7 (t, C=CH$_2$); 127.9, 128.5 (d, *o*-C + *m*-C); 132.6 (d, *p*-C); 137.6 (s, *i*-C); 138.4 (d, CH=C); 199.8 (s, CO)

[a] The I.R. spectra were recorded on a Perkin-Elmer M 225 as liquid films; the strongest absorptions only are given.

[b] The ^{1}H-N.M.R. spectra were recorded on a Jeol J NM-MH-100-Spectrometer for C$_6$D$_6$ solutions (compounds **a–i**) or CDCl$_3$ solutions (compounds **j–n**) at 100 MHz using TMS as internal reference.

[c] The ^{13}C-N.M.R. spectra were recorded on a Varian C.F.T. 20-Spectrometer for C$_6$D$_6$ solutions (compounds **a–i**) or CDCl$_3$ solutions (compounds **j–n**) at 20 MHz using TMS as internal reference; multiplicities given are from off-resonance spectra.

[d] Diastereomeric mixture, nearly 1 : 1.

[e] Aliphatic carbon atoms without assignment.

all cases with high regioselectivity to yield the enamines **6** only. Since the lithioallylsilane is alkylated in the 3-position only[10], the regioselectivity in **5** is controlled by the presence of the amino group.

3-Oxosilanes 7; General Procedure:

Method A: To a solution of the silylenamine **4** (5 mmol) in tetrahydrofuran (20 ml) under an argon atmosphere at 0 °C is added, using a syringe dropwise with stirring, a solution of *n*-butyllithium (5.5 mmol; in cases **a–d**, 7.5 mmol) in hexane (~3.5/~4.8 ml) and then hexamethylphosphoric triamide (2 ml).

Method B: To a suspension of the silylenamine **4** (5 mmol) and potassium *t*-butoxide (0.52 g, 5.5 mmol) in 30–50 °C petroleum ether (15 ml) under an argon atmosphere at 0 °C is added, using a syringe dropwise with stirring, *t*-butyllithium (5.5 mmol) in pentane (~3.5 ml).

In both methods, after stirring for the time given in Table 1, the alkyl halide (5.5 mmol) is added using a syringe and the mixture is again stirred at 0 °C for the time given in Table 1. Then, water (20 ml) is added, the organic layer separated, diluted with ether (20 ml), and stirred with 4 normal hydrochloric acid (20 ml) for 14 h **(7a–d)**, or 24 h **(7g–i)** at room temperature, or for 8 h **(7h–n)** under reflux. Then dichloromethane (20–25 ml) is added, the organic layer separated, washed twice with water (15 ml), dried with anhydrous sodium sulfate, the solvent removed using a rotary evaporator, and the residue distilled using a kugelrohr oven. [The yields given in Table 1 refer to the analytically pure products so obtained.]

Silylenamines 4:

1-(N-Methyl-N-phenylamino)-3-phenyl-3-trimethylsilyl-1-propene **(4b)** is prepared from **1b** according to Ref.[11] and *1-(N-methyl-N-phenylamino)-1-phenyl-3-trimethylsilyl-1-propene* **(4d)** from **1d** according to Ref.[1].

1-(N-Methyl-N-phenylamino)-3-trimethylsilyl-1-propene **(4a)**[12]: To 1-(*N*-methyl-*N*-phenylamino)-2-propene (**2a**; 1.47 g, 10 mmol) and potassium *t*-butoxide (1.1 g, 11 mmol) in *t*-butyl methyl ether (30 ml) under an argon atmosphere at −78 °C is added, using a syringe dropwise with stirring, *t*-butyllithium (11 mmol) in pentane (~7 ml). After 2 h at −78 °C, chlorotrimethylsilane (1.2 g, 11 mmol) is added using a syringe. After 15 min, the mixture is allowed to come to room temperature, washed three times with water (20 ml), dried with anhydrous sodium sulfate, and, after removing the solvent using a rotary evaporator, the residue is distilled with a kugelrohr oven to give a pale yellow liquid; yield: 1.86 g (85%); b.p. 70 °C/0.05 torr. For analytical data, see Ref.[12].

^{1}H-N.M.R. (C_6D_6/TMS): $\delta = -0.05$ (s, 9H); 1.36 (dd, 2H, $J = 8.5$ Hz, 1.5 Hz); 2.75 (s, 3H); 4.85 (dt, 1H, $J = 8.0$ Hz, 8.5 Hz); 5.78 (dd, 1H, $J = 8.0$ Hz, 1.5 Hz); 6.6–7.3 ppm (m, 5H).

^{13}C-N.M.R. (C_6D_6/TMS): $\delta = -1.96$ [q, $Si(CH_3)_3$]; 19.6 (t, CH_2); 35.2 (q, CH_3); 112.9 (d, NCH=CH—); 116.4 (d, *o*-C); 119.7 (d, *p*-C); 129.3 (d, *m*-C); 132.5 (d, NCH=CH—); 148.3 ppm (s, *i*-C).

2-Methyl-1-(N-methyl-N-phenylamino)-3-trimethylsilyl-1-propene **(4c)**[13]:

To 1-(*N*-methyl-*N*-phenylamino)-2-methyl-1-propene (**1c**; 1.61 g, 10 mmol) and potassium *t*-butoxide (1.1 g, 11 mmol) in 50–70 °C petroleum ether (40 ml) under an argon atmosphere at 0 °C is added, using a syringe dropwise with stirring, *t*-butyllithium (11 mmol) in pentane (~7 ml). After 3 h at 0 °C, chlorotrimethylsilane (1.2 g, 11 mmol) is added using a syringe. After 1 h, ether (30 ml) and water (25 ml) are added. The organic layer is washed twice with water (25 ml), dried with anhydrous sodium sulfate, and, after removing the solvent using a rotary evaporator, the residue is distilled to give a pale yellow liquid; yield: 1.38 g (59%); b.p. 75–77 °C/0.01 torr.

$C_{14}H_{23}NSi$	calc.	C 72.03	H 9.93	N 6.00
(233.4)	found	71.67	9.93	6.01

^{1}H-N.M.R. (C_6D_6/TMS): $\delta = -0.03$ (s, 9H); 1.46 (br s, 2H); 1.58 (d, 3H, $J = 1.3$ Hz); 2.73 (s, 3H); 5.53 (br s, 1H); 6.6–7.4 ppm (m, 5H).

^{13}C-N.M.R. (C_6D_6/TMS): $\delta = -0.6$ [q, $Si(CH_3)_3$]; 21.7 (q, CCH_3); 22.5 (t, CH_2Si); 38.6 (q, NCH_3); 113.4 (d, *o*-C); 117.7 (d, *p*-C); 126.7 (s, C=C—CH_3); 128.0 (d, CH=C); 129.1 (d, *m*-C); 149.2 ppm (d, *i*-C).

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