1,4-*N,C*-Elimination of trialkylsilanol as a new way of fragmentation of *N,N*-bis(trialkylsilyloxy)enamines

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N,N-Bis(trialkylsilyloxy)enamines (BSENA), obtained recently by the double silylation of nitroalkanes,[1–3] react with N- [1] and C-nucleophiles[2] and rearrange under the action of Lewis acids or upon heating to bistrialkylsilyl derivatives of α-hydroxyoximes.[1,3]

We found that BSENA containing the X—CH_2— substituent (X is the electron-withdrawing group) at the C(2) atom are capable of undergoing a new type of fragmentation under the action of bases: 1,4-*N,C*-elimination of trialkylsilanol to form trialkylsilyl derivatives of unsaturated α,β-oximes.

The new fragmentation of BSENA was performed by the transformation of methyl 4-*N,N*-bis(trimethylsilyloxy)aminobut-3-enonate (**3**) to methyl 4-trimethylsilyloxyiminobut-2-enonate (**4**) (Scheme 1). Derivative **4** can be obtained both without isolation of intermediate BSENA **3** under conditions of silylation of the initial nitro compound **1** at a higher temperature (see Scheme 1, stage *c* in comparison with stage *a*), and by treatment of enamine **3** with triethylamine (see Scheme 1, stage *b*).

Desilylation of compound **4** by methanol gives stable methyl 4-hydroxyiminobut-2-enonate (**5**). Oximes **4** and **5** in $CDCl_3$ exist as a mixture of *E-anti*-, *E-syn*-, and *Z-anti*-isomers (**a**, **b**, and **c**, respectively). The configurations of oximes **5** were established by NMR (Gated, $^1H—^1H$, and $^{13}C—^1H$ correlations) and by the comparison of the chemical shifts and spin coupling constants of oximes **5** (Table 1) with the corresponding parameters of methylacrylate and isomers of cinnamic acid.[4]

The fragmentation found can be used for the development of a two-stage method for stereoselective β-hydroxyiminoalkylation of compounds with the conjugated double bond.

Methyl 4-*N,N*-bis(trimethylsilyloxy)aminobut-3-enonate (**3**). Yield 67%. ^1H NMR ($CDCl_3$, relative to $SiMe_4$), δ: 0.18 (s, 18 H, $SiMe_3$); 3.03 (dd, 2 H, CH_2, ^3J = 8 Hz, ^4J = 1 Hz); 3.70 (s, 3 H, OMe); 5.60 (dt, 1 H, CH, ^3J = 14 Hz); 6.06 (dd, 1 H, CH—N). ^{13}C NMR ($CDCl_3$, relative to $SiMe_4$), δ: 0.88 ($SiMe_3$); 35.21 (CH_2); 52.79 (MeO); 114.29 (CH); 145.95 (CH—N); 172.42 (C=O). ^{29}Si NMR (INEPT, $CDCl_3$, $SiMe_4$), δ: 24.39.

Methyl 4-trimethylsilyloxyiminobut-2-enonate (**4**). Yield 71% (calculated per nitro compound **1** at stage *c*), b.p. 46–50 °C (0.5 Torr), n_D^{20} 1.4760. The ratio **4a** : **4b** : **4c** = 4.0 : 1.0 : 1.3 (according to ^1H NMR spectra).

Methyl 4-hydroxyiminobut-2-enonate (**5**). Yield 97%, m.p. 92–94 °C (from CH_2Cl_2—pentane). The ratio **5a** : **5b** : **5c** = 4.0 : 1.0 : 1.3 (according to ^1H NMR spectra). Found (%): C, 45.79; H, 5.26; N, 10.97. $C_5H_7NO_3$. Calculated (%): C, 46.51; H, 5.47; N, 10.85.

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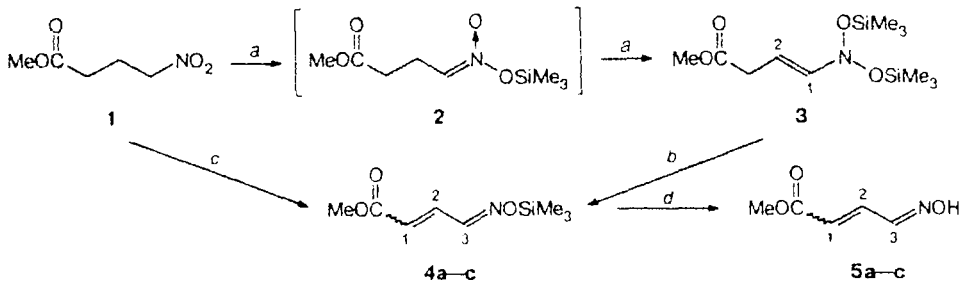
Scheme 1



Reagents and conditions: *a*. Me_3SiBr/Et_3N (**1** : Me_3SiBr : Et_3N = 1 : 2.03 : 2.02, mol/mol) in $ClCH_2CH_2Cl$, −28 °C, 96 h; *b*. Et_3N in $ClCH_2CH_2Cl$, −28 °C; *c*. Me_3SiBr/Et_3N (**1** : Me_3SiBr : Et_3N = 1 : 3.3 : 3.4, mol/mol) in $ClCH_2CH_2Cl$, −15 °C → 10 °C, 48 h; *d*. MeOH (excess), NH_4F, 15 °C.

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Table 1. Parameters of ^1H, ^{13}C, and ^{29}Si NMR spectra (INEPT) for products **4** and **5** (in $CDCl_3$)

Product	Conformation	δ ^1H [a] ($^3J_{H,H}$/Hz)					δ ^{13}C [a] ($^3J_{H,H}$/Hz)						δ ^{29}Si [a]
		H(1) (d)	H(2) (dd)	H(3) (d)	MeO (s)	$SiMe_3$ (s)	C(1)	C(2)	C(3)	MeO	C=O	$SiMe_3$	
4a	*E-anti*	6.15	7.37, 10	7.93, 16	3.78	0.27	126.37	138.04	152.87	51.63	166.06	−1.08	28.25
4b	*E-syn*	6.17	7.86, 10	7.42, 17	3.80	0.27	127.22	129.96	149.60	51.77	166.10	−1.08	27.78
4c	*Z-anti*	6.01 (^4J = 1)[b]	6.69, 10	8.95, 12	3.76	0.27	122.56	137.49	152.36	51.36	166.01	−1.08	27.61
5a	*E-anti*	6.16	7.34, 10	7.87, 16	3.75	—	126.04 (dt),[c] 164	138.35 (dd),[c] 161	149.05 (dd),[c] 166	51.97	166.78	—	—
5b	*E-syn*	6.18	7.84, 10	7.26, 16	3.76	—	127.21 (dt),[c] 164	129.92 (dd),[c] 165	145.86 (dd),[c] 178	51.99	166.78	—	—
5c	*Z-anti*	6.01 (^4J = 1)[b]	6.69, 9	8.88, 13	3.74	—	122.44 (d),[c] 166	137.59 (dd),[c] 159	148.52 (dd),[c] 173	51.66	166.78	—	—

[a] Relative to $SiMe_4$.
[b] The existence of the constant ^4J is additional evidence for the *Z*-configuration of the C=C bond.[5]
[c] The multiplicity and spin coupling constants of ^{13}C NMR signals were determined by the Gated procedure.

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