Registry No. **1a**, 105336-81-0; **1b**, 105336-82-1; **1c**, 105336-83-2; **1d**, 105336-84-3; **1e**, 105336-85-4; **2a**, 105371-89-9; **2b**, 105371-90-2; **2c**, 5700-45-8; **2d**, 105371-91-3; **2e**, 105371-92-4; **3a**, 105371-93-5; **3b**, 105371-94-6; **3c**, 105371-95-7; **3d**, 105371-96-8; **3e**, 105371-97-9; **4a**, 4705-34-4; **4b**, 1142-15-0;)4c, 5043-91-4; **4d**, 52364-50-8; **5a**, 41097-47-6; **5b**, 41097-54-5; **5c**, 105399-71-1; $C_6H_{11}CH_3$, 2043-61-0; *P*-$(OCH_3)C_6H_4COH$, 123-11-5; PhCHO, 100-52-7; *p*-ClC_6H_4CHO, 104-88-1; *p*-$(CN)C_6H_4CHO$, 105-07-7.

A Novel Synthesis of 2-Siloxazolidines by 1,5-Elimination from 1-(Trimethylsiloxy)-2-(*N*-substituted-*N*-(methoxydimethylsilyl)amino)ethanes

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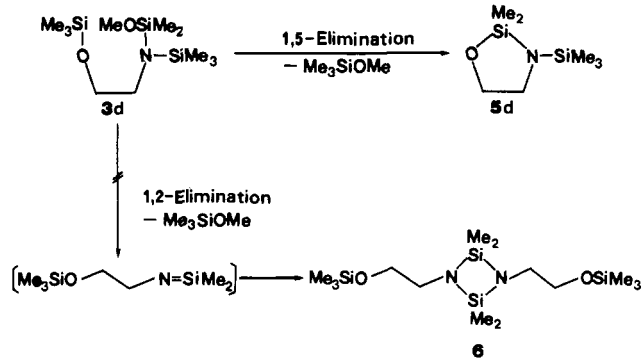
Summary: The vacuum sealed tube thermolyses of $Me_3SiOCH_2CH_2NRSiMe_2(OMe)$ (R = Me, Ph, $SiMe_3$) gave new heterocyclic compounds, 2,2,3-trimethyl-2-siloxazolidine, 2,2-dimethyl-3-phenyl-2-siloxazolidine, and 2,2-dimethyl-3-(trimethylsilyl)-2-siloxazolidine, through the 1,5-elimination of trimethylmethoxysilane, respectively. These 2-siloxazolidine derivatives reacted easily with methanol to give ring-cleavage products.

It has been anticipated that 5-membered heterocyclic compounds containing a N–Si–O moiety would be readily synthesized via reactions of bifunctional silanes with ethanolamine derivatives. However, all attempts to synthesize the 2-siloxazolidines have been unsuccessful to date,[1] although 2-siloxazolidones[2] and 2,2-dimethyl-3-oxa-2-silaindoline[3] were prepared from the reaction of bifunctional silanes with amino acid derivatives and *o*-aminophenol, respectively. We have recently become interested in synthesizing 2-siloxazolidines having a N–Si–O bond and their thermal and chemical properties. In this communication we wish to report the preparation and properties of these new heterocyclic compounds, 2-siloxazolidines. Considering that the 2-siloxazolidines could be formed from a ring-closure reaction through an intramolecular transalkoxylation,[4] 1-(trimethylsiloxy)-2-(*N*-substituted-*N*-(methoxydimethylsilyl)amino)ethanes (**3a–d**) were prepared. The reactions of dimethylmethoxychlorosilane (**2**) with (2-(*N*-substituted amino)ethoxy)trimethylsilanes (**1a** and **1b**) gave compounds **3a**[5] and **3b**[6] in 48 and 49% yields, respectively (eq 1). Compounds **3c**[7] and **3d**[8] were obtained in 45 and 66% yields, respectively, after the aminoethoxytrimethylsilanes (**1c** and **1d**) were lithiated with *n*-butyllithium at −78 °C and **2** was subsequently added at 0 °C (eq 2).

Scheme I



$$\underset{\substack{\mathbf{1a},\ R = H\\ \mathbf{1b},\ R = Me}}{Me_3SiOCH_2CH_2NHR} + \underset{\mathbf{2}}{Me_2Si(OMe)Cl} \xrightarrow[-B\cdot HCl]{B} \underset{\substack{\mathbf{3a},\ R = H\\ \mathbf{3b},\ R = Me}}{Me_3SiOCH_2CH_2NRSiMe_2(OMe)} \quad (1)$$

$$\underset{\substack{\mathbf{1c},\ R = Ph\\ \mathbf{1d},\ R = SiMe_3}}{Me_3SiOCH_2CH_2NHR} \xrightarrow[\text{ii. } Me_2Si(OMe)Cl,\ 0\ ^\circ C]{\text{i. } n\text{-BuLi, } -78\ ^\circ C} \underset{\substack{\mathbf{3c},\ R = Ph\\ \mathbf{3d},\ R = SiMe_3}}{Me_3SiOCH_2CH_2NRSiMe_2(OMe)} \quad (2)$$

It is of interest to note that each of the products **3a–d** was purely isolated from the corresponding reaction mixtures by the vacuum distillation method without any ring-closure reaction which might have happened.[4] In contrast, Zhdanov and co-workers[4] reported that the reaction mixture of dimethylmethoxy(chloromethyl)silane with **1a** and **1c** gave the 2,2-dimethyl-2-silamorpholine derivatives **4** during the vacuum distillation and strongly suggested that 1,6-elimination of trimethylmethoxysilane occurred under this condition as shown in eq 3.

$$Me_3SiOCH_2CH_2NHR + ClCH_2SiMe_2(OMe) \xrightarrow[-B\cdot HCl]{B} \quad R = H,\ Ph$$

$$Me_3SiOCH_2CH_2NRCH_2SiMe_2(OMe) \xrightarrow{-Me_3SiOMe} \underset{\mathbf{4}}{\text{R-N(CH}_2\text{)}_2\text{-SiMe}_2\text{-O}} \quad (3)$$

In order to lead 1,5-elimination of trimethylmethoxysilane from the precursors **3a–d**, the vacuum sealed tube thermolysis (VSTT) method was adapted. When **3d** dissolved in cyclohexane was subjected to VSTT at 300 °C for 3 h, **3b** was completely consumed with the formation

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(5) Compound **3a**: bp 71–72 °C (7 torr); ^1H NMR (CCl_4) δ 0.01 (s, 6 H), 0.02 (s, 9 H), 1.2 (s, 1 H), 2.83 (d of t, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 8.2 Hz, 2 H), 3.39 (s, 3 H), 3.51 (t, $^3J_{HH}$ = 5.5 Hz, 2 H).
(6) Compound **3b**: bp 80–81 °C (10 torr); ^1H NMR (CCl_4) δ 0.05 (s, 6 H), 0.08 (s, 9 H), 2.52 (s, 3 H), 2.85 (t, $^3J_{HH}$ = 6.0 Hz, 2 H), 3.33 (s, 3 H), 3.52 (t, $^3J_{HH}$ = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −2.94, 0.00, 35.08, 50.08, 53.01, 61.49. Anal. Calcd for $C_9H_{25}O_2NSi_2$: C, 45.90; H, 10.70; N, 5.95. Found: C, 45.74; H, 10.50; N, 5.93.
(7) Compound **3c**: bp 117–118 °C (4 torr); ^1H NMR (CCl_4) δ 0.03 (s, 9 H), 0.19 (s, 6 H), 3.43 (s, 3 H), 3.49 (s, 4 H), 7.08 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −1.42, 0.05, 49.88, 50.38, 61.70, 121.26, 121.74, 129.51, 148.70. Anal. Calcd for $C_{14}H_{27}O_2NSi_2$: C, 56.51; H, 9.15; N, 4.71. Found: C, 56.45; H, 9.08; N, 4.74.
(8) Compound **3d**: bp 79–80 °C (4 torr); ^1H NMR (CCl_4) δ 0.08 (s, 9 H), 0.15 (s, 15 H), 2.93 (m, 2 H), 3.35 (m, 2 H), 3.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ −1.02, 0.00, 1.24, 45.88, 50.00, 65.51. Anal. Calcd for $C_{11}H_{31}O_2NSi_3$: C, 44.99; H, 10.64; N, 4.77. Found: C, 44.60; H, 10.99; N, 4.79.

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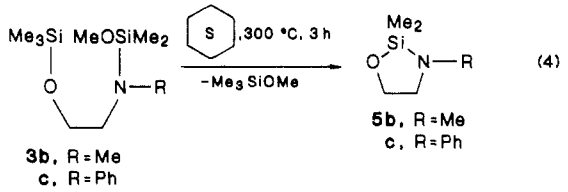
Table I. Vacuum Sealed Tube Thermolysis Experiments of $Me_3SiOCH_2CH_2NRSiMe_2(OMe)$

reactant R	conditions: temp, °C	time, h	% decomp	product	yield, %
H (3a)	250	3	100		
	300	3	100		
Me (3b)	300	3	100	5b	65
Ph (3c)	300	3	100	5c	95
$SiMe_3$ (3d)	300	3	85	5d	85
	300	8	100	5d	95
	350	3	100	5d	95

of the expected heterocyclic compounds 2,2,3-trimethyl-2-siloxazolidine (**5b**)[9] and trimethylmethoxysilane as



(4)

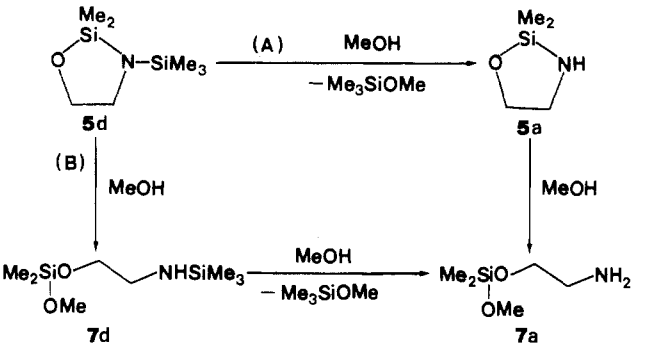
transalkoxylation products along with some other minor products. And when **3c** was also subjected to VSTT at the same condition as above, almost all of the starting material was pyrolyzed to give quantitatively the heterocyclic compound 2,2-dimethyl-3-phenyl-2-siloxazolidine (**5c**),[10] which was a colorless liquid at 0 °C (eq 4).

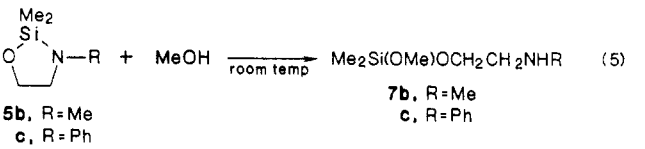
The VSTT of precursor **3d** was carried out at 350 °C for 3 h to increase the percent decomposition of starting material (85% decomposition at 300 °C). In this condition compound **3d** was completely pyrolyzed to give quantitatively the heterocyclic compound 2,2-dimethyl-3-(trimethylsilyl)-2-siloxazolidine (**5d**).[11] Interestingly we have not observed cyclodisilazane (**6**) which was expected as a silanimine dimer product as shown in Scheme I. This result indicates that the 1,5-elimination of trimethylmethoxysilane is favored over the 1,2-elimination[12] under this condition. The results of the experiments for **3a–d** are summarized in Table I.

When 3a was treated similarly at 250 and 300 °C, respectively, for 3 h, almost all of **3a** was consumed, giving various unidentified products without any formation of the expected ring-closure product 2,2-dimethyl-2-siloxazolidine (**5a**). This indicates that **5a** might be thermally unstable, although compounds **5b–d** were stable under these thermolysis conditions. The thermostability of compounds **5b–d** were observed in the control experiments carried out under this thermolysis conditions.

The silicon–nitrogen bond in the 2-siloxazolidine could be readily cleaved with alcohols to give ring-cleavage products.[2] We have observed that both **5b** and **5c** were readily reacted with equimolar amount of absolute methanol in dry cyclohexane at room temperature to give the expected ring-cleavage products dimethylmethoxy(2-(*N*-methylamino)ethoxy)silane (**7b**) and dimethylmethoxy(2-anilinoethoxy)silane (**7c**), respectively (eq 5).

Scheme II





(5)

However, the alcoholysis of **5d** in the presence of an equimolar amount of methanol gave the products dimethylmethoxy(2-aminoethoxy)silane (**7a**) and trimethylmethoxysilane with unreacted **5d** instead of **5a** and **7d** as shown in Scheme II. These products were believed to arise from the desilylation reaction of **5d** and followed by ring cleavage (pathway A) or reverse order (pathway B). Scheme II illustrates the possible reaction pathway proposed for formation of product **7a**. More work is now in progress to clarify the mechanism of this interesting methanolysis reaction.

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Registry No. **1a**, 5804-92-2; **1b**, 98156-23-1; **1c**, 16403-21-7; **1d**, 17165-52-5; **2**, 1825-68-9; **3a**, 105857-32-7; **3b**, 105694-22-2; **3c**, 105694-23-3; **3d**, 105694-24-4; **5b**, 86426-95-1; **5c**, 105694-25-5; **5d**, 105694-26-6; **7a**, 105694-28-8; **7b**, 105694-27-7; **7c**, 27247-86-5.

(9) Compound **5b**: mp 73–75 °C; ^1H NMR (CCl_4) δ 0.15 (s, 6 H), 2.61 (s, 3 H), 2.91 (t, $^3J_{HH}$ = 4.2 Hz, 2 H), 3.63 (t, $^3J_{HH}$ = 4.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -3.35, 36.11, 53.92, 60.03; mass spectrum, *m/e* 131 (M^+), 130 ($M^+ - H$), 116 ($M^+ - CH_3$). Anal. Calcd for $C_5H_{13}ONSi$: C, 45.75; H, 9.98; N, 10.67. Found: C, 45.06; H, 10.00; N, 10.37.

(10) Compound **5c**: ^1H NMR (CCl_4) δ 0.36 (s, 6 H), 3.26 (t, $^3J_{HH}$ = 6.3 Hz, 2 H), 4.05 (t, $^3J_{HH}$ = 6.3 Hz, 2 H), 6.4–7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.11, 46.92, 64.04, 114.87, 118.26, 129.97, 147.64; mass spectrum, *m/e* 193 (M^+), 178 ($M^+ - CH_3$). Anal. Calcd for $C_{10}H_{15}ONSi$: C, 62.12; H, 7.82; N, 7.25. Found: C, 61.20; H, 7.83; N, 7.17.

(11) Compound **5d**: ^1H NMR (CCl_4) δ 0.01 (s, 9 H), 0.12 (s, 6 H), 3.00 (t, $^3J_{HH}$ = 6.0 Hz, 2 H), 3.86 (t, $^3J_{HH}$ = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.25, 2.36, 46.97, 65.56; mass spectrum, *m/e* 189 (M^+), 174 ($M^+ - CH_3$). Anal. Calcd for $C_7H_{19}ONSi_2$: C, 44.39; H, 10.11; N, 7.39. Found: C, 43.55; H, 9.89; N, 7.14.

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Coordinatively Unsaturated Clusters: The Rapid Reversible Addition of Two Carbonyl Ligands to a Trinuclear Platinum Cluster

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Summary: The complexes $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (M = Pt or Pd; dppm = $Ph_2PCH_2PPh_2$) add CO rapidly and reversibly at room temperature to give $[M_3(\mu_3\text{-CO})(CO)(\mu\text{-dppm})_3]^{2+}$ and, when M = Pt, $[M_3(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_3]^{2+}$, but the halide adducts $[M_3(\mu_3\text{-X})(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{+}$ (X = Cl, Br, or I) do not add extra CO ligands; this reversible addition of two ligands to a coordinatively unsaturated cluster without cluster breakdown is a novel feature and allows a closer cluster–surface analogy than in earlier model systems.

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