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SYNTHESIS AND THERMAL REACTIONS OF 3-TRIMETHYLSILYL-1-PYRAZOLINE

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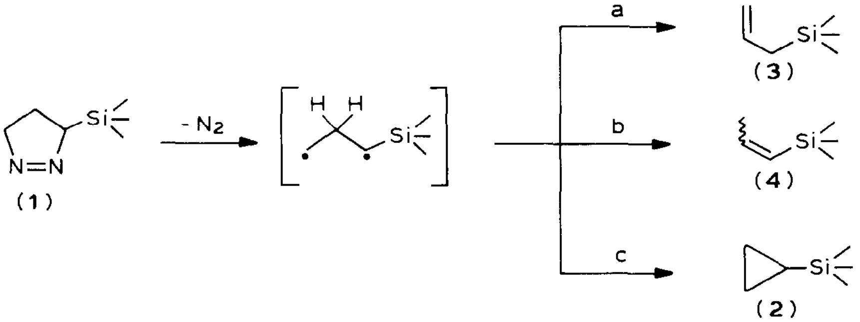
Summary

The compound 3-trimethylsilyl-1-pyrazoline has been synthesized by addition of diazomethane to vinyltrimethylsilane at room temperature. In contrast, addition of trimethylsilyldiazomethane to ethylene at 55°C yields 1-trimethylsilyl-2-pyrazoline exclusively. The thermal isomerization of 3-trimethylsilyl-1-pyrazoline to 1-trimethylsilyl-2-pyrazoline has been followed kinetically by proton NMR spectroscopy and the reverse reaction has been detected by gas phase pyrolysis. Thermal elimination of nitrogen from either pyrazoline leads to cyclopropyltrimethylsilane, allyltrimethylsilane and *E*- and *Z*-1-propenyltrimethylsilane. The relative rates of methylene-H migration to radical centers α and γ to silicon are approximately equal.

Introduction

In the course of kinetic studies of the thermal isomerization of cyclopropyltrimethylsilane [1], we have investigated reactions of 3-trimethylsilyl-1-pyrazoline (**1**). This ring structure was chosen in anticipation that extrusion of dinitrogen would



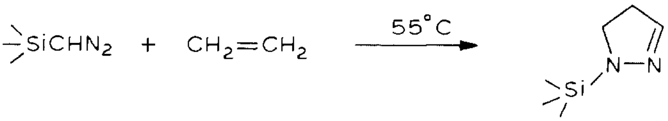
produce a 1,3-biradical (diyl) with radical centers α and γ to the silicon substituent [2]. Of particular interest was the effect of the metalloid atom on the relative rates of methylene-H migration to the non-equivalent radical centers (path a and path b).

Previous reports of variously substituted silylpyrazolines [3–5] suggested that cycloaddition of either trimethylsilyldiazomethane to ethylene or diazomethane to vinyltrimethylsilane would provide the desired substrate. Among these, however, one study showed that a 4-silylpyrazoline, the wrong regioisomer for our purposes, can be the major product of the diazomethane approach and only in that work were thermal reactions studied [5].

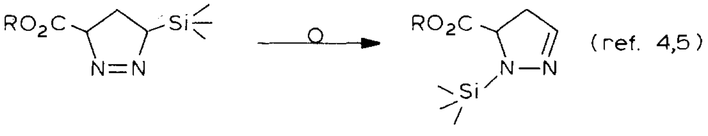
In this paper we report two different synthetic approaches to **1**, a facile isomerization of the trimethylsilyl group from C to N as well as the first example of the reversibility of this reaction and the relative rates of hydrogen migration to radical centers α or γ to a silicon atom in the thermal reaction.

Results and discussion

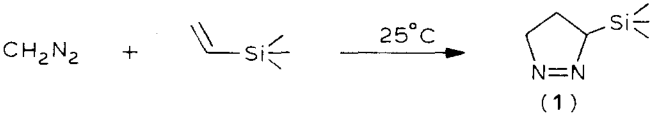
Our initial attempts to synthesize the 3-silylpyrazoline via a 1,3-dipolar addition of trimethylsilyldiazomethane to an ethereal solution of ethylene were unsuccessful. After 39 d at room temperature, no decoloration of the yellow-green solution occurred and chromatographic analysis showed no product formation. In a less polar solvent such as pentane, the reaction at 55°C was complete within 13 d but spectral analysis indicated exclusive formation of 1-trimethylsilyl-2-pyrazoline (**5**) instead of the desired 1-isomer. Precedent for 1,3 silyl shifts from C to N over a pyrazoline ring comes from the work of Brook [4] and Cunico [5].



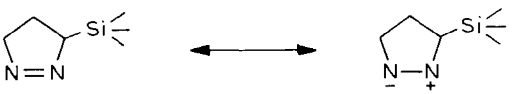
(**5**)



Synthesis of 3-trimethylsilyl-1-pyrazoline was accomplished by the addition of diazomethane to vinyltrimethylsilane at room temperature. The remarkable propensity of silylpyrazolines to isomerize suggested caution in a structural assignment [3–6]. All spectroscopic data (^1H, ^{13}C NMR; IR; UV; GC/MS and exact mass) are consistent with the proposed structure. An interesting feature of ^{13}C chemical shifts for the non-equivalent carbon atoms, both α to the azo linkage, is that the one attached to silicon is further downfield (82.91 ppm, OFR doublet) than the methylene carbon (74.91 ppm OFR triplet). A possible rationale for this phenomenon is an unexpectedly large contribution from the polar resonance form II to I. Stabilization of a positive charge β to silicon is well-known [7] and the required decrease in electron density on the adjacent nitrogen could deshield the methyne carbon [8].

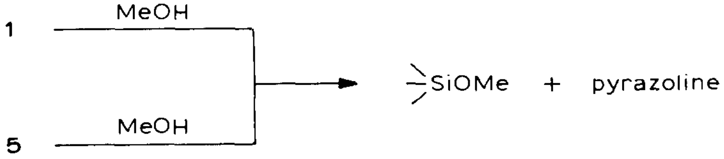


(**1**)



(I) (II)

Further chemical studies based on the sensitivity of both **1** and **5** to moisture assisted in the structure determination. Addition of dry methanol to samples of **1** and to **5** produced a rapid exothermic reaction leading to methoxytrimethylsilane and 1- or 2-pyrazoline. The silane was identified by comparison of GLC retention times and mass spectra with an authentic sample while the pyrazoline, which could be either isomer, was identified by GC/MS.



Since **1** and **5** are easily distinguished by ^{1}H NMR, the rearrangement could be monitored conveniently at 65°C by measuring peak areas of the trimethylsilyl group attached to silicon or nitrogen. The resulting plot of $\ln([\mathbf{1}_0]/[\mathbf{1}_f])$ for **1** and **5** vs. time showed good first order kinetics and suggests that the isomerization is most probably a unimolecular process. In a separate experiment at the relatively low temperature where the kinetics of **1** to **5** were followed, the reverse reaction, **5** to **1**, could not be detected. Since both the C=N π bond and the Si–N σ bond energies of the product are significantly larger than the N=N π and Si–C σ bond energies of the reactant [9], we expect the isomerization to be exothermic.

Gas phase pyrolysis of **1** at 342°C (300 s) in a conventional fused-salt reactor afforded a mixture of organic products: cyclopropyltrimethylsilane (**2**) (47.3%), allyltrimethylsilane (**3**) (2.7%), both *E* and *Z* 1-propenyltrimethylsilane (**4**) (2.5%), unreacted **1** and **5** (47.3%) and small amounts of an unidentified oxygenated silane (< 5%) present in the starting material. Pyrolysis of **5** at the same temperature (300 s) yielded nearly the same product distribution. At higher temperatures, 442°C for 600 s, thermal decomposition of either **1** or **5** led to complete decomposition but the

TABLE 1

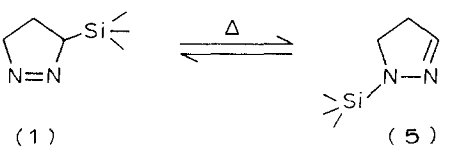
PYROLYSIS OF 1 AND 5 [a]

T (°)	*t* (s)	Substrate	Unreacted **1**+**5** [b]	**2**	**3**	**4** [c]	**3**/**4**
342	300	**1**	44.6	47.3	2.7	2.5	1.1
342	300	**5**	46.2	46.2	2.8	1.8	1.6
442	600	**1**	4.4	34.6	6.3	3.7	1.7
442	600	**5**	2.7	47.9	9.5	5.0	1.9

[a] All pyrolyses were repeated at least twice and reported percentages are averages. Experimental error is ±5%. [b] On the SP 2100 column where baseline separation of **2**, **3**, **4** and the oxygenated impurity was achieved, **1** and **5** had identical retention times. [c] Yields of *E*- and *Z*-propenyltrimethylsilanes are combined.

low mass balance (70–80%) suggests that some polymerization occurred. Moreover, under these conditions significant decomposition of cyclopropyltrimethylsilane also occurred (20%) and the reaction products cannot be attributed exclusively to the primary events of pyrazoline decomposition.

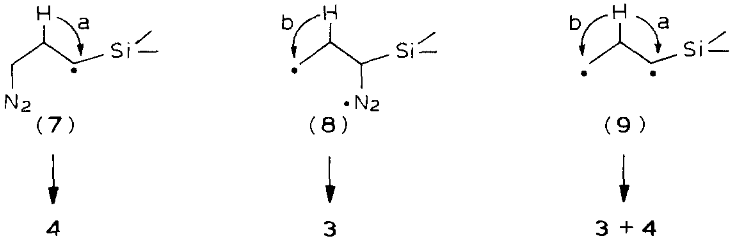
Formation of the same products from both **1** and **5** at 342°C and the demonstration that **1** isomerized to **5** at lower temperature strongly suggests that the *C*- and *N*-silylated pyrazolines had reversibly isomerized prior to nitrogen loss. To our knowledge this is the first example of a silyl migration from N to C [10].



(1) (5)

As noted above, the main reaction channel for 3-trimethylsilylpyrazoline decomposition was ring closure to cyclopropyltrimethylsilane **2** and the minor pathway led to the olefins, allyltrimethylsilane **3** and *E*- and *Z*-propenyltrimethylsilane **4**. Since **2** was stable under the reaction conditions (342°C, 300 s), olefins **3** and **4** likely arise from some species other than the cyclopropane. Additional support for this conclusion is the difference in the distribution of olefinic products from **1** and from **2**. An earlier study [11] of the flow pyrolysis of **2** at 450°C indicated 95% yield of **3**. Fragmentation of **1** at 341°C, however, yields relatively much more internal olefin, **3**/**4** = 1.1.

The immediate precursor(s) to products **3** and **4** and even **2** from **1** remains obscure as does a detailed mechanism of any pyrazoline decomposition [2]. There are several possible species along the reaction pathway to final products. Fragmentation of the unsymmetrical pyrazoline may proceed by stepwise cleavage of either C–N bond (**7** and **8**) or by direct formation of the 1,3-diyl (**9**).



(7) (8) (9)

Although the data do not permit us to differentiate between the stepwise and concerted elimination of nitrogen, the distribution of products offers insight to the relative rates of H-migration to radical centers α and γ to silicon. Should stepwise cleavage occur, generation of **7** and **8** appears equally likely as there is little evidence for any difference in stability of the two radical centers. Thus products **4** and **3** would be indicative of relative rates of H-migration to the nonequivalent radical sites. If **9** were formed, the product analysis again would suggest relative rates of paths a and b. Despite these mechanistic uncertainties, both stepwise and concerted pyrazoline fragmentation require that the H shift to radical centers α and γ to a trimethylsilyl group occur with nearly statistical probability.

Experimental

General data

Proton NMR spectra were recorded on a Hitachi Perkin–Elmer R24B 60-MHz spectrometer using methylene chloride as an internal standard and carbon NMR spectra were obtained on a JEOL FX 90Q spectrometer with D_2O or $CDCl_3$ as a lock solvent. All chemical shifts are reported in ppm downfield from external tetramethylsilane. Infrared spectra were recorded in gas phase cells with approximately 10 torr of sample on a Perkin–Elmer 1330 spectrometer calibrated to polystyrene. Preparative gas chromatography was performed on a Varian 90A GLC (thermal conductivity detector). When reaction products were not isolated, yields were calculated from response factors using cyclohexane as an internal standard. Analytical gas chromatography was performed on a HP 5840A GLC (flame ionization detector) equipped with a Valco gas sampling port. Mass spectra were determined on a HP 5970A mass selective analyzer coupled to a HP 5790A gas chromatograph. Exact mass measurements were determined at the Midwest Center for Mass Spectrometry.

E- and *Z*-1-propenyltrimethylsilane was synthesized by the method of Seyferth and Vaughn [12] and cyclopropyltrimethylsilane was synthesized by addition of vinyltrimethylsilane to the Simmons–Smith reagent prepared by the method of Rawson and Harrison [13].

3-Trimethylsilyl-1-pyrazoline (1)

A round bottom flask with smooth joints was fitted with a thermometer and mechanical stirrer both in cork stoppers. To the flask was added 30 g of a 40% solution of potassium hydroxide and 100 ml of decalin. The two phase mixture was then chilled to 0°C and a safety shield was placed in front of the flask. A total of 10 g (0.10 mole) of *N*-nitrosomethylurea [14] was added to the flask in 0.5 g portions at such a rate that the reaction temperature did not exceed 5°C. The mixture was stirred for an additional 20 min and the bright yellow organic layer was quickly decanted into a glass cylinder (3 × 25 cm) cooled in a dry ice/isopropanol slush bath. Vapors of diazomethane were swept by nitrogen (5cc/min) from the decalin solution into a 10 cm vessel containing a teflon-coated stirring bar and 2 g (20 mmol) of vinyltrimethylsilane. In order to minimize evaporative loss, a spiral condenser, cooled to 0°C, and a cold finger, held at −78°C were attached to the reaction vessel. After 6 h, transfer of the gaseous diazomethane was nearly complete as indicated by diminution of the bright yellow color. During this period the entire system was shielded from light to eliminate the formation of methylene.

Preparative GLC on an OV-17 (20% on Chromobsorb W 45/60, 1/4 in. × 2 1/2 ft., detector temp. 110°C, injector temp. 105°C, oven temp 65°C and flow rate 65 cc/min) indicated one major peak. A total of 1.4 g (57% yield based on the amount of vinyltrimethylsilane) was isolated by GLC collection. UV (cyclohexane) λ_{max} 320 nm (ϵ 536); ^{13}C NMR (neat) δ −0.37 (q), 82.91 (d), 18.51 (t), 74.91 (t); ^1H NMR (neat) δ 0.34 (9H, s, $(CH_3)_3Si$), 1.11 (2H, m), 3.88 (3H, br m); IR (gas) 2940–2840s, 1535m, 1490m, 1440m, 1250s, 850s, 760s cm^{-1}; *m/e* (relative intensity) 142 (41), 127 (91), 100 (19), 73 (100), 59 (95), 43 (52); exact mass calcd. for $SiC_6H_{14}N_2$ 142.0927, found 142.0925.

1-Trimethylsilyl-2-pyrazoline (5)

Initial attempts to purify **1** on a 22 ft. OV-17 (20% on Chromobsorb W) column at 65°C led to complete isomerization to **5**. UV (cyclohexane) λ_{max} 250 nm (ϵ 9836); ^{13}C NMR (neat) δ −1.95 (q), 44.35 (t), 33.28 (t), 137.67 (d); ^{1}H NMR (neat) δ −0.24 (9H, s, $(CH_3)_3Si$), 2.91 (2H, app t, CH_2N), 2.18 (2H, m, CH_2CH), 6.03 (1H, t, J 10.1 Hz); IR (gas) 3040m, 2940–2840s, 1550s, 1470m, 1440m, 1250m, 950s, 850s, 760s, 635m cm^{-1}; m/e (relative intensity) same as **1**; exact mass calcd. for $SiC_6H_{14}N_2$ 142.0927, found 142.0926.

Attempted syntheses of 3-trimethylsilyl-1-pyrazoline

Trimethylsilyldiazomethane [15] (0.5 g, 4 mmol) was added to a pentane (3 ml) solution of excess ethylene after which the reaction bulb was sealed. After gentle warming for 13 d at 55°C the characteristic diazo color nearly disappeared. Preparative GLC on the 22 ft. OV-17 afforded 0.31 g (54% yield) of **5**. Under very similar reaction conditions with an ethereal solution of trimethylsilyldiazomethane, no discernable change occurred and GLC analysis indicated no reaction.

Thermolysis of 1

A sealed tube of **1** (neat) was immersed in a silicone oil bath held at 65°C and removed periodically for NMR analysis. Concentration of **1** was monitored by the peak area under the trimethylsilyl signal vs. time: 78 (0 min); 61 (325); 41 (995); 35 (1516); 18.5 (2353). A plot of $\ln([\mathbf{1}_0]/[\mathbf{1}_f])$ against time indicated good first order kinetics (correlation coefficient = 0.993). Given the imprecise nature of the reaction conditions, we attach little significance to the absolute value of k: 5.85×10^{-4} min^{-1}. Of importance is that the first order plot suggests that the reaction is unimolecular. The same experimental conditions did not produce any measurable reaction of **5**.

Pyrolysis of 1

To an evacuated 250 ml quartz reaction vessel in a fused-salt bath held at 342°C by a proportional thermal regulator (GCA Precision Scientific Model 1053A thermotrol) vapors of 1 (4.1 torr) were introduced and removed after 300 by condensation to a gas sampling bulb cooled by liquid nitrogen. Analysis of the contents of the heated sampling bulb on a 10% SP 2100 column (1/8 in × 10 ft.) indicated the following products: **2** (47.3%), **3** (2.7%), *E*- and *Z*-**4** (2.5) and unreacted **1** and **5** (44.6%). Similarly, pyrolysis of **5** (4.5 torr) yielded **2** (46.2%), **3** (2.8%), **4** (1.8%) and **1** and **2** (46.2%). On the SP-2100 column where baseline separation of reaction products and the oxygenated silane was obtained, **1** and **5** had identical retention times. Blank experiments showed negligible isomerization of **2**, **3** and **4** at this time and temperature.

Acknowledgement

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