Notes

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Figure 1. ORTEP drawing of 40% probability displacement elipsoide. Hydrogen atoms are omitted for clarity. And parameters for disordered atoms are the mean values.

racter. Clearly the acetate ligand is bonded to Y in an isobidentate type from the same distances of Y-O(19) and Y-O(20) within experimental error.

Supplementary Material Available. Tables of atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms (2 pages), bond distances and angles (2 pages), anisotropic displacement parameters (2 pages), hydrogen coordinate and isotropic displacement parameters (1 pages), and observed and calculated structure factors (17 pages) are available from J. H. J..

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Thermal Rearrangement of 3-Trimethylsilyl-1-Pyrazoline

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Several examples of 1,3- and 1,5-rearrangement of a silyl group to a heteroatom have been reported. These comprise 1,3-migrations from carbon to oxygen,[1] nitrogen to oxygen,[2] nitrogen to nitrogen,[2b,3] nitrogen to sulfur,[2b] and 1,5-migrations from oxygen to oxygen[4] and nitrogen to nitrogen.[5] The unimolecular reaction kinetics of a suprafacial 1,3-sigmatropic rearrangement involving an antisymmetric 3p silicon orbital of silyl group in allylsilanes has been reported.[6] There is a precedent for 1,3-trimethylsilyl shift from carbon to nitrogen over a pyrazoline ring.[7~10] Cycloaddition of diazomethane to vinyltrimethylsilane would provide the desired starting material, 3-trimethylsilyl-1-pyrazoline, 1.[10] During the course of purification of 1 on a preparative GC with an OV-17 (20% on Chromosorb W 80/100, 1/4 in×22 ft) the complete isomerization to 1-trimethylsilyl-2-pyrazoline, 2 was discovered. To our knowledge, the kinetics of 1,3-silyl group migration from carbon to nitrogen over a pyrazoline ring has not reported yet.

We wish to report the kinetics of thermally induced 1,3-rearrangement of a trimethylsilyl group from carbon to nitrogen over a pyrazoline ring. The isomerization of 1 to 2 has been examined kinetically by means of ^{1}H NMR spectroscopy. The effect of solvent on the rate of rearrangement from 1 to 2 has been briefly considered. Thermal elimination of dinitrogen from 3-trimethylsilyl-1-pyrazoline leads to cyclopropyltrimethylsilane, allyltrimethylsilane, and *E*- and *Z*-propenyltrimethylsilane at higher temperatures (417-478 °C).[11] However, thermolysis of 1 in a sealed capillary tube at lower temperatures (70-100 °C) leads to 2 without decomposition of the starting material, 1.

1 **2**
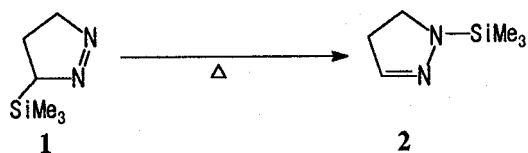
Since **1** and **2** are easily distinguished by ^{1}H NMR, the rearrangement could be examined conveniently by measuring peak height of the trimethylsilyl group attached to carbon or nitrogen on the pyrazoline ring. A plot of $\ln([2]_t/[2]_0)$ *vs.* time(min) provides good first order kinetics (correlation coefficient=0.998) and suggests that the isomerization is most probably an unimolecular process. The compound **2** did not isomerize to the compound **1** at the same experimental conditions which means the reverse process (**2**→**1**) is more energetic. Since both the C=N π bond and the Si-N σ bond energies of the product **2** are significantly larger than the N=N π bond and Si-C σ bond energies of the starting material **1**,[12] we expect this 1,3-rearrangement of silyl group from carbon to nitrogen of **1** to be exothermic process. The rate constants and activation parameters for the thermal isomerization of **1** to **2** are listed in Table 1.

The negative values of the activation entropy (Table 1) are consistent with the previously proposed four-centered cyclic intermediate or transition state, as opposed to a homolytic or heterolytic dissociation and recombination mechanism.[8,13-16] It is obvious that the rates of rearrangement of **1** to **2** is affected by the solvent polarity. A high degree of solvent participation in the transition state must be involved. The cleanly first-order kinetics and the entropies of activation, which range from −19.2 to −29.5eu on the solvent polarity, are consistent with an unimolecular reaction involving a cyclic intermediate or transition state with charge separation. On this basis it is probably reasonable to assume a pentacoordinate silicon intermediate involving d-orbital participation in the thermal isomerization of **1** to **2**. The transition state for the 1,3-migration of silyl group was represented as follows.
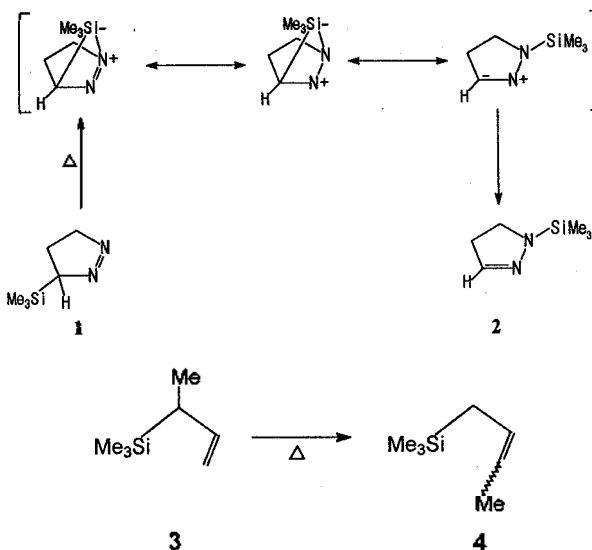
The activation energy of 18.4 kcal/mol and entropy of activation of −19.2eu for the conversion of **1** to **2** *via* 1,3-migration of trimethylsilyl group from carbon to nitrogen are compared to E_a=47.7 kcal/mol and $\Delta s^\ddagger$ = −6.2eu for the isomerization of α-methylallyltrimethylsilane, **3** to γ-methylallyltrimethylsilane,[6] **4** *via* 1,3-migration of trimethylsilyl group from

3 **4**

carbon to carbon.

A similar entropy of activation, $\Delta s^\ddagger$ = −34.2eu, was reported for the conversion of Ph$_3$SiC(OH)MePh to siloxane.[17] Rate measurements for Me$_3$SiCH$_2$COPh had shown a change in activation energy from 30.6 to 22.9 kcal and in entropy of activation from +2.7 to −14.9eu on changing the solvent composition from pure benzene to nitrobenzene/benzene (4 : 1 v/v).[14] This was clear evidence for an intermediate or transition state with charge separation.

Experimental

^{1}H NMR spectra were recorded on a Bruker AW80 spectrometer using TMS as an internal standard and ^{13}C NMR spectra were obtained on the spectrometer with CDCl$_3$ as a lock solvent. Mass spectra were obtained on a Shimadzu GCMS-QP 1000A coupled to a Schimadzu GC-9A gas chromatograph. Preparative gas chromatography was performed on a Varian model 920GLC (thermal conductivity detector) using an OV-17 (20% on Chromosob W 80/100)column. UV spectra were recorded on Shimadzu UV-265 spectrophotometer. Solvents were dried before use in the kinetic studies.

A solution of approximately 0.3 g of the pyrazoline, **1** was prepared in about 0.3 mL of dried benzene or nitromethane. Aliquots of 40 µL were sealed in ten capillary tubes. At t=0, all but one of the samples were placed together in the silicon oil bath and the clock started. At specified time intervals (min), a sealed capillary tube was taken out from the bath and cooled in ice-water to stop the reaction. The rearrangement of **1** to **2** was monitored conveniently measuring peak height of the trimethylsilyl group attached to carbon or nitrogen on the pyrazoline ring by means of ^{1}H NMR spectroscopy. At least 3 scans were made to obtain an average value for the peak height. The peak height of the solvent was used to calibrate the instrument response.

Preparation of 3-Trimethylsilyl-1-pyrazoline (1). A round bottom flask with not ground-glass joints was fitted with a thermometer and a 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 cooled to 0 ℃ and a safety shield

Table 1. Rate Constants and Activation Parameters for 1,3-Trimethylsilyl Rearrangement of 3-Trimethylsilyl-1-pyrazoline[a]

Temp ℃	$k \times 10^3$ min^{-1} (benzene)	Temp ℃	$k \times 10^{-3}$, min^{-1} (nitromethane)
70	2.578	70	12.75
80	4.634	80	21.36
90	10.15	90	38.50
100	22.25	100	63.47

E_a=18.4± 0.2 kcal/mol E_a=13.7± 0.3 kcal/mol
$\Delta S^\ddagger_{85}$= −19.2± 0.6 eu $\Delta S^\ddagger_{85}$= −29.5± 0.8 eu
logA=9.10± 0.12   logA=6.85± 0.17

[a] E_a and $\Delta S^\ddagger$ at 85 ℃ calculated by least square programs

was placed in front of the flask. A total of 10 g (0.10 mol) of *N*-nitrosomethylurea[18] was added to the flask in 0.5 g portions at such a rate that the reaction temperature did not exceed 5 ℃. The mixture was stirred for an additional 20 min and the bright yellow organic layer was quickly decanted into a glass tube (3×25 cm) cooled in a dry ice/acetone bath. Vapors of diazomethane were swept by nitrogen gas (5 mL/min) from the decalin solution into a 10 cm branched glass vessel containing a stirring bar and 2 g (20 mmol) of vinyltrimethylsilane.[19] A spiral condenser, cooled to 0 ℃, and a cold finger, kept at −78 ℃ were attached to the branched glass vessel. After 6h, introduction of the gaseous diazomethane was nearly complete as indicated by diminution of the bright yellow color.

Preparative GC on an OV-17 (20% on Chromosorb W 80/100, 1/4 in×2 ft; detector temp., 110 ℃; injector temp., 105 ℃; oven temp., 65 ℃; flow rate, 65 mL/min) appeared one major peak. A total of 1.4 g (57% yield based on the amount of vinyltrimethylsilane) was isolated. UV (cyclohexane): λ_{max} 320 nm (ε 536); ^{1}H NMR (neat): δ 0.34 (s, 9H, Si(CH$_3$)$_3$), 1.11 (m, 2H), 3.88 (br m, 3H); ^{13}C NMR (neat) δ: −0.37 (q), 82.91 (d), 18.51 (t), 74.91 (t); MS m/z 142 (M$^+$, 41), 127 (91), 100 (19), 73 (100), 59 (95), 43 (52).

1-Trimethylsilyl-2-pyrazoline (2). Purification of **1** by a preparative GC on a 22 ft OV-17 (20% an Chromosorb W) column at 80 ℃ led to complete isomerization to **2**. UV (cyclohexane): λ_{max} 250 nm (ε 9836); ^{1}H NMR (neat): δ −0.24 (s, 9H, Si(CH$_3$)$_3$), 2.91 (app t, 2H, CH$_2$N), 2.18 (m, 2H, CH$_2$ CC), 6.03 (t, 1H, J=10.1 Hz HC=N); ^{13}C NMR (neat) δ: −1.95 (q), 44.35 (t) , 33.28 (t), 137.67 (d); MS m/z same as **1**.

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Luminescence Characteristics of Y$_2$O$_2$S : Eu^{3+}, Tb^{3+} Phosphor

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An inorganic phosphor basically consists of a host lattice in which activator ions are incorporated. These ions usually determine the energy levels responsible for the luminescence process.[1] When lanthanide(III) ions are incorporated into the insulating ionic host as an activator, characteristic 4f-4f transition sharp line spectra are resulted. Because of the shielding nature by the outer filled orbitals, perturbation by surrounding neighbors is negligible and the spectral characteristics are nearly independent of the host lattice.

The red emitter Eu^{3+} activated yttrium oxysulfide, Y$_2$O$_2$S : Eu^{3+}, has been widely used in cathode ray tubes (CRT) for color TVs and color monitors because of its high efficiency and brightness.[2~7] The characteristics and the efficiency of Y$_2$O$_2$S : Eu^{3+} luminescence have been extensively studied since it has been introduced by Royce.[2,3] The Y$_2$O$_2$S : Eu^{3+} surpasses the (Zn, Cd)S : Ag (red 670 nm) in cathodoluminescence (CL) efficiency by 30% and the YVO$_4$: Eu^{3+} in brightness by 40%. The energy level diagram for Eu^{3+} in Y$_2$O$_2$S is shown in Figure 1(a). Stimulation by photons (absorption λ_{max}=365 nm; photoluminescence; PL) or high energy elect-

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