THERMAL REARRANGEMENT OF *N*-SILYLMETHYLATED AZADIENES TO *N*-SILYLATED 2-PYRROLINES

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Summary: N-Silylmethylated 1-azadienes thermally rearranged to N-silylated 2pyrrolines, which were readily hydrolyzed to 1-pyrrolines on workup. Formation of the N-silylated pyrrolines strongly suggested that the intramolecular cyclization proceeded via a 1,3-dipolar intermediate formed by the thermal 1,2-shift of the silyl group onto the nitrogen atom of the azadienes.

N-Silylmethylated imines are often reported to be good precursors of azomethine ylides, most of which are generated via quaternization followed by desilylation.¹⁻³) We previously reported the novel thermal rearrangement of aryl-substituted N-(silylmethyl)imines to 2,3-diarylaziridines with high cisselectivity,⁴) where 1,2-silicon shift leading to N-silyl azomethine ylide intermediates proceeded.



The aziridines were clarified to be formed by hydrolysis of the corresponding N-silylated aziridines. Thus this reaction was claimed to occur via N-silylated azomethine ylide intermediates formed by the thermal 1,2-shift of the silyl group onto the nitrogen atom and not by a trace of H₂O actable as a quaternization-desilylation catalyst.³)

Here we report the thermal rearrangement of N-silylmethylazadienes into pyrroline derivatives in the manner of the 1,2-silicon shift. Though either or both of two products, an alkenylaziridine and a pyrroline, were expected in this reaction, only N-silylated pyrroline was formed in high yield.

A typical reaction procedure is as follows. $1-(\alpha-Trimethylsilyl)benzyl-1-aza-1,3-butadiene$ (1a: 1.0 mmol) was refluxed in toluene (7 ml) for 5 h under nitrogen atmosphere. The products were separated by preparative TLC on SiO₂ to give

trans-4,5-diphenyl-1-pyrroline (3a) in 55% yield. The results of thermal treatment of the other N-silylmethylazadienes 1b and 1c leading to the corresponding pyrrolines are listed in Table 1.



The structure of pyrroline **3a** was identified by spectral data and elemental analysis, and *trans* configuration was determined by the coupling constant between H-4 and H-5 in the ¹H-NMR spectrum. The isolated pyrroline **3a** did not contain trimethylsilyl group at all, which was similar to the case with the ready hydrolysis of N-silylaziridines.⁴)

Table 1. Thermal rearrangement of azadienes

azadiene	solvent	temp.	time	yield(%)	
		(°C)	(h)	2*	3
<u>1</u> a	benzene	80	5	0	0
1 a	toluene	110	5	97	55
1 b	xylene	110	48	0	0
1 b	xylene	140	48	55	30
1 c	xylene	140	40	79	42
		1			

* determined by ¹H-NMR

When the rearrangement of N-silylmethylazadiene 1a in d6-benzene was monitored in a sealed tube at 110 °C by ¹H-NMR, a set of signals corresponding to 1-trimethylsilyl-4,5-diphenyl-2-pyrroline (2a) were observed.⁵) But the generation of the expected 1,3-dipolar intermediate was not detected. After 5 h the N-silylpyrroline 2a was formed almost quantitatively (97%) with high stereoselectivity (*cis/trans* = 1/5). The silylpyrroline 2a was found to be very sensitive to moisture and rapidly converted to 3a under air.⁶) As N-Si bond is easily hydrolyzed, it is clear that the desilylation of 2a by water and isomerization during the workup gave rise to 1-pyrroline 3a. The lower isolated yield of 3a as compared to that of 2a is probably because of further hydrolysis of 3a during chromatography, but byproducts could not be identified.

Thermal rearrangement of 1a proceeded in refluxing toluene, but not in refluxing benzene. Dienes 1b and 1c needed higher reaction temperatures. It is noticeable that the diene 1b has no aryl substituent on the silylmethyl group $(R^{1}=H)$ as an azomethine ylide-stabilizing group. Formation of N-silylated pyrrolines 2b and 2c in good yields was confirmed by ¹H-NMR⁵) in all cases.

It is reasonable to assume the 1,3-dipolar intermediate 4 as a precursor of 1silyl-2-pyrroline 2, similarly to the rearrangement of silylmethylimines to silylaziridines. To trap the dipolar intermediate, 1a was refluxed in toluene for 5 h in the presence of N-phenylmaleimide. As a major product, the bicyclic compound 5a was obtained along with the desilylated compound 6a in 51% total yield. The compound 5a was a 1:1 adduct of the expected intermediate 4a and the maleimide; 1-trimethylsilylated structure of 5 was clearly supported by ¹H-NMR and also by mass spectrometry (M⁺: m/z = 466). The formation of very small amounts of stereoisomers³,⁷) of 5a and 6a⁸) was detected by ¹H-NMR. These results strongly supported the intermediacy of the N-silylated 1,3-dipole 4a.



5a: R = TMS, 6a: R = H

Difference in stereochemical courses leading to trans-2a and cis-2c as major products needs further study, but a plausible interpretation at the moment is illustrated as follows. The isomerization of 1 is initiated by the thermal shift of trimethylsilyl group onto the vicinal nitrogen atom to generate the 1,3-dipolar (or 1,5-dipolar) intermediate 4. The intermediate 4 is in equilibrium with its geometrical isomers and the 6π systems, E-4 and Z-4, thermally cyclize in disrotatory fashion to trans-2 and cis-2, respectively. The intermediate E-4 is expected when R = H because of the steric repulsion between trimethylsilyl group and phenyl group, but contribution of Z-4 increases when R = Me because of repulsion between methyl group and phenyl group.



References and Notes

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- 3) O. Tsuge, S. Kanemasa, A. Hatada, and K. Matsuda, Bull. Chem. Soc. Jpn., 59, 2537 (1986), and references cited therein.
- 4) M. Komatsu, M. Ohno, S. Tsuno, and Y. Ohshiro, Chem. Lett., 1990, 575.
- 5) Spectral data for 2a-c are as follows; 2a (trans:cis = 84:16); trans-2a: ¹H-NMR (C6D6) δ -0.12 (s, 9H, SiMe3), 3.89 (ddd, J = 1.7, 2.7, 4.6 Hz, 1H, H-4), 4.50 (d, J = 4.6 Hz, 1H, H-5), 4.69 (dd, J = 3.9, 2.7 Hz, 1H, H-3), 6.31 (dd, J = 3.9, 1.7 Hz, 1H, H-2), 6.8-7.3 (m, 10H, Ph); ¹³C-NMR (C6D6) ppm -0.4 (SiMe3), 61.1 (d, C-4), 73.0 (d, C-5), 101.7 (d, C-3), 137.4 (d, C-2); cis-2a: ¹H-NMR (C6D6) δ 0.07 (s, 9H, SiMe3), 4.5 (m, J is not certain, 1H, H-4), 4.7 (m, J is not certain, 1H, H-3), 4.92 (d, J = 11.2 Hz, 1H, H-5), 6.37 (dd, J = 3.9, 2.0 Hz, 1H, H-2); 2b: ¹H-NMR (C6D6) δ -0.06 (s, 9H, SiMe3), 3.15 (dd, J = 6.8, 10.5 Hz, 1H, H-5), 3.60 (dd, J = 11.2, 10.5 Hz, 1H, H-5'), 3.94 (dddd, J = 1.9, 2.2, 11.2, 6.8 Hz, 1H, H-4), 4.23 (dd, J = 3.7, 2.2 Hz, 1H, H-3), 6.08 (dd, J = 3.7, 1.9 Hz, 1H, H-2); ¹³C-NMR (C6D6) ppm -0.4 (SiMe3), 49.9 (t, C-5), 56.2 (d, C-4), 103.6 (d, C-3), 137.2 (d, C-2); 2c
- $(trans:cis = 38:62); trans-2c: {}^{1}H-NMR (C_6D_6) \delta 0.07 (s, 9H, SiMe_3), 1.67 (dd, J = 1.3, 1.4 Hz, 3H, Me), 3.74 (ddq, J = 1.6, 4.7, 1.4 Hz, 1H, H-4), 4.68 (d, J = 4.7 Hz, 1H, H-5), 6.21 (dq, J = 1.6, 1.3 Hz, 1H, H-2); cis-2c: {}^{1}H-NMR (C_6D_6) \delta 0.11 (s, 9H, SiMe_3), 1.76 (dd, J=1.3, 1.4 Hz, 3H, Me), 4.36 (ddq, J = 1.6, 11.5, 1.4 Hz, 1H, H-4), 5.15 (d, J = 11.5 Hz, 1H, H-5), 6.29 (dq, J = 1.6, 1.3 Hz, 1H, H-2).$
- 6) Spectral data for **3a-c** are as follows; **3a**: ¹H-NMR (CDCl₃) δ 2.5-3.4 (m, 3H, H-3, -4), 5.0-5.2 (m, 1H, H-5), 6.1-7.6 (m, 10H, Ph), 7.8-7.9 (m, 1H, H-2); ¹³C-NMR (C₆D₆) ppm 46.8 (t, C-3), 51.3 (d, C-4), 84.3 (d, C-5), 166.2 (d, C-2); MS (m/z) 221 (M⁺), 194 (M⁺-N=CH), 178 (PhC=C-Ph), 144 (M⁺-Ph), 117 (M⁺-PhCH=CH₂); IR (Nujol) 1604 cm⁻¹; **3b**: ¹H-NMR (C₆D₆) δ 2.31-4.45 (m, 5H, H-3, -4, -5), 6.9-7.5 (m, 5H, Ph), 7.61 (br s, 1H, H-2); MS (m/z), 145 (M⁺); IR (Nujol) 1662 cm⁻¹; **3c** (mixture of stereoisomers, **3c**₁:**3c**₂ = 54:46); **3c**₁: ¹H-NMR (CDCl₃) δ 1.22 (d, J = 6.7 Hz, 3H, Me), 2.9-3.6 (m, 1H, H-3), 3.37 (dd, J = 8.3, 8.3 Hz, 1H, H-4), 5.53 (ddd, J = 8.3, 2.2, 1.9 Hz, 1H, H-5), 6.6-7.5 (m, 10H, Ph), 7.93 (ddd, J = 1.9, 1.6 Hz, 1H, H-2); MS (m/z) 235 (M⁺); **3c**₂: ¹H-NMR (CDCl₃) δ 1.22 (d, J = 6.7 Hz, 3H, Me), 2.67 (dd, J = 8.7, 8.7 Hz, 1H, H-4), 2.9-3.6 (m, 1H, H-3), 5.09 (ddd, J = 8.7, 2.6, 2.6 Hz, 1H, H-5), 6.6-7.5 (m, 10H, Ph), 7.68 (ddd, J = 2.6, 2.6 Hz, 1H, H-2); MS (m/z) 235 (M⁺).
- 7) O. Tsuge, K. Ueno, and K. Oe, Bull. Chem. Soc. Jpn., 59, 1809 (1986); Heterocycles, 19, 1411 (1982).
- 8) Spectral data for 6a are as follows; ¹H-NMR (CDCl₃) δ 3.68 (d, J = 6.5 Hz, 1H, -PhCHC<u>H</u>(CO)-), 3.72 (dd, J = 7.1, 7.8 Hz, 1H, -HNC<u>H</u>(CH=)-), 4.44 (dd, J = 7.8, 6.5 Hz, 1H, -HNCH(CH=)C<u>H</u>-), 5.07 (broad s, 1H, -HNC<u>H</u>Ph-), 6.35 (dd, J = 7.1 Hz, 16.3 Hz, 1H, =CH-), 6.80 (d, J = 16.3 Hz, 1H, PhC<u>H</u>=); MS (m/z), 394 (M⁺); IR (KBr), 1714, 1780 cm⁻¹.

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