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Stereoselective Synthesis of *cis*-2,3-Diarylaziridine by Rearrangement of Aryl-Substituted *N*-(Silylmethyl)imine

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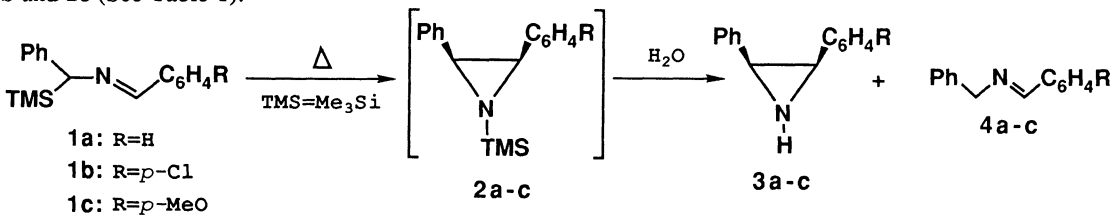
Thermal rearrangement of aryl-substituted *N*-(silylmethyl)imines to *N*-silyl-aziridines with high *cis*-selectivity was revealed and workup of the products readily led to *cis*-aziridine derivatives.

N-Silylmethylated imines are often reported to be good precursors of azomethine ylides, whose generation is usually performed by quaternarization of the imines followed by desilylation.[1] Here we wish to report the novel thermal rearrangement of aryl-substituted *N*-(silylmethyl)imines to 2,3-diarylaziridines with high *cis*-selectivity,[2] which features the formation of azomethine ylide directly via the silicon 1,2-shift. Aziridines are of great interest because of their synthetic applicability.[3]

N-(α-Trimethylsilylbenzyl)benzylideneamine (**1a**) was refluxed in xylene for 24 h followed by column chromatography (SiO_2) to give *cis*-2,3-diphenylaziridine (**3a**)[4] in 63% (82% based on the converted **1a**) and the desilylated imine **4a** (14%). The reaction is highly stereoselective and no *trans*-isomer was detected. Similarly, unsymmetrically disubstituted *cis*-aziridines **3b** and **3c** could be prepared selectively from *N*-silylmethylimines **1b** and **1c** (See Table 1).[5]



1a: R=H
1b: R=*p*-Cl
1c: R=*p*-MeO

2a-c **3a-c** **4a-c**

While the yield of aziridine **3a** increased at higher reaction temperature and with longer reaction period, the selectivity of **3a** slightly decreased after 24 h because of an increase in the desilylated imine **4a**. The rearrangement of silylmethylimine **1a** to aziridine **3a** is more favorable in nonpolar solvents and does not need any desilylation reagent such as CsF. The sole example of azomethine ylide formation from an *N*-silylmethylated imine without such desilylating agent is that in HMPA-H_2O media reported by Tsuge et al.[1b]

When the rearrangement of imine **1a** at 140 °C in d_6-benzene was monitored by ^{1}H-nmr, a new set of signals corresponding to those of *cis*-*N*-trimethylsilyl-2,3-diphenylaziridine (**2a**)[6] appeared and increased with a decrease in the amount of **1a** and the reaction ceased after 8 h. When the nmr tube was opened to air, silyl-aziridine **2a** was readily converted to *cis*-aziridine **3a**. Furthermore, an azomethine ylide, a precursor of silyl-aziridine **2a**, was trapped with diethyl acetylene dicarboxylate (DEAD) to give pyrroline **5** (in 43% as a 7:3

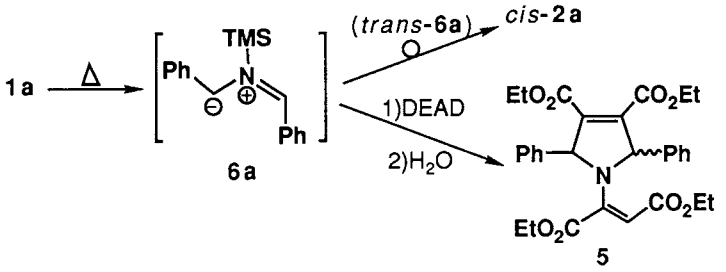
mixture of *cis* and *trans* isomers)[7] by heating imine **1a** in the presence of DEAD[8] followed by SiO_2 chromatography.

Table 1. Thermal Rearrangement of Imines **1** to Aziridines **3**

Imine **1**	R	Solvent	Additive	Temp	Time h	Yield or Recovery/% **3**	**4**	**1**
1a	H	benzene	--	reflux	24	0	0	96
1a	H	toluene	--	reflux	24	17(44)[a]	22	61
1a	H	xylene	--	reflux	5	49(93)	3	48
1a	H	xylene	--	reflux	15	55(95)	2	42
1a	H	xylene	--	reflux	24	63(82)	14	23
1a	H	MeCN	--	reflux	24	0	0	100
1a	H	THF	--	reflux	24	0	0	100
1a	H	THF	CsF(1eq)	rt	10	0	100	0
1a	H	HMPA	H_2O(1eq)	rt	36	0	53	0
1b	*p*-Cl[b]	xylene	--	reflux	24	57(73)	--[c]	22
1c	*p*-MeO[b]	xylene	--	reflux	24	43(74)	--[c]	42

a) Yields in parentheses are based on the reacted **1**.
b) The starting imine contains a regioisomer [Ph-CH=NCH(Ar)TMS] in 30% for **1b** and 10% for **1c**.
c) Not determined.

Thus the intermediate azomethine ylide **6a**, formed by rearrangement of the silyl group onto the nitrogen atom, is assumed to cyclize to *N*-silyl *cis*-aziridine **2a**. In the scheme on the right, the most stable (**6a**) of four possible geometrical forms is depicted and thermal conrotatory cyclization of this *trans*-**6a** would give rise to *cis*-**2a**.



References

1) See for example; a) E. Vedejes and G. R. Martinez, *J. Am. Chem. Soc.*, **102**, 7993 (1980); K. Achiwa, T. Motoyama, and M. Sekiya, *Chem. Pharm. Bull.*, **31**, 3939 (1983); T. Livinghouse and R. Smith, *J. Org. Chem.*, **48**, 1554 (1983); A. Padwa, G. Hoffmanns, and M. Tomas, *Tetrahedron Lett.*, **24**, 4303 (1983); O. Tsuge, S. Kanemasa, S. Kuraoka, and S. Takenaka, *Chem. Lett.*, **1984**, 279, 281; b) O. Tsuge, S. Kanemasa, A. Hatada, and K. Matsuda, *Bull. Chem. Soc. Jpn.*, **59**, 2537 (1986), and references cited therein.

2) Stereoselective synthesis of *cis*-substituted aziridines has not been so extensively studied because of various limitations; see Ref. 3.

3) See for example; A. Padwa and A. D. Woolhouse, "Aziridines, Azirines, and Fused-ring Derivatives," in "Comprehensive Heterocyclic Chemistry," ed by W. Lwowski, Pergamon Press, Oxford (1984), Vol. 7.

4) The *cis*-structure of **3a** was determined by identification with an authentic sample: Y. Diab, A. Laurent, and P. Mison, *Bull. Soc. Chim. Fr.*, **1974**, 2202.

5) Spectral data for **3b,c** (isolated with SiO_2 column) are as follows; **3b**: mp 79 °C; NMR ($CDCl_3$) δ 1.50 (s, NH), 3.01 (d, J = 0.3 Hz, CH), 3.12 (d, J = 0.3 Hz, CH), 7.1-7.5 (m, 9H); MS *m/z* 231 (M^+); **3c**: mp 65 °C; NMR ($CDCl_3$) δ 1.60 (s, 1H, NH), 3.49 (s, 2 x CH), 3.70 (s, Me), 7.0 (m, 9H); MS *m/z* 225 (M^+).

6) The compound **2a** was prepared by reaction of Me_3SiCl and lithium salt of **3a**; NMR (C_6D_6) δ 0.10 (s, Me), 3.21 (s, CH), 7.0 (m, Ph).

7) **5**: IR (neat) 1740, 1730, 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.83 (t, 3H), 1.03 (t, 6H), 1.10 (t, 3H), 3.69 (q, 4H), 3.93 (q, 4H), 4.48 (s, 0.7H, *cis*-CH=), 4.67 (s, 0.3H, *trans*-CH=), 5.78 (s, 0.6H, 2 x *trans*-CH), 6.04 (s, 1.4H, 2 x *cis*-CH), 7.0-7.5 (m, 10H); MS *m/z* 535 (M^+). When **5** (*cis* : *trans* = 7 : 3 mixture) was treated with NaH in refluxing Et_2O for 4 h and quenched with H_2O, *cis*-**5** was exclusively obtained (87% yield).

8) Insertion of DEAD to a Si-N bond is known: T. A. George and M. F. Lappert, *J. Organomet. Chem.*, **14**, 327 (1968).

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