Journal of Organometallic Chemistry, 152 (1978) C25—C28
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

BIS(SILYL)ENAMINES OR SILYLAZIRIDINES FROM THE THERMAL REACTIONS OF AZIDES WITH ALKENYLSILANES

ALAN R. BASSINDALE[*], ADRIAN G. BROOK, PETER F. JONES and JAMES A.G. STEWART

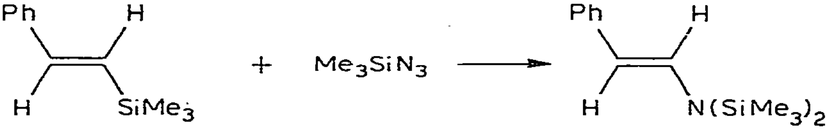
Department of Chemistry, University of Toronto, Toronto, M5S 1A1 (Canada)

(Received January 30th, 1978)

Summary

When vinylsilanes and other alkenylsilanes react with silyl azides the products were found to be bis(silyl)enamines, presumably arising from thermal rearrangement of intermediate triazolines. Other azides react with alkenylsilanes to give triazolines, which fail to rearrange to silylenamines, but which instead yield silylaziridines.

Our discovery of the thermal rearrangements of silylepoxides [1] prompted us to investigate the behaviour of silylaziridines. Following a report that the reaction of vinyltriethylsilane with trimethylsilyl azide gave triethylsilyl-*N*-trimethylsilylaziridine as the sole product [2], we heated together *trans*-trimethylsilyl azide under reflux for 5 days and isolated, in 55% yield, not the expected aziridine but instead *trans*-*N*,*N*-bis(trimethylsilyl)aminostyrene (I)[**], b.p. 82—84°C/0.05 mmHg, the first reported *N*,*N*-bis(silyl)enamine; IR (CCl_4): 6.2 μm (C=C); NMR: δ 5.78, 6.62 ppm (2H, 2d, AB system, J 14 Hz). No intermediate cycloaddition products could be detected when the reaction was run under a variety of conditions monitored by NMR.



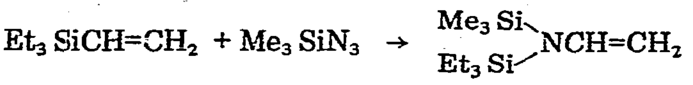
(I)

---

[*] Present address: The Chemistry Department, The Open University, Milton Keynes, Bucks. (Great Britain).

[**] Acceptable analyses for this and other new compounds were obtained: e.g. Anal. Found: C, 63.98; H, 9.64; N, 5.25. $C_{14}H_{25}NSi_2$ calcd.: C, 63.80; H, 9.56; N, 5.31%.

This surprising finding led us to repeat the reaction of vinyltriethylsilane with trimethylsilyl azide under various conditions. In all cases, including the conditions of the original report (10 days heating to 125°C), the product obtained, whose spectral properties were incompatible with an aziridine, was found to be *N*-triethylsilyl-*N*-trimethylsilylaminoethene (II). b.p. 48—50°C/ 1 mmHg. IR: 6.2 μm (C=C); NMR: δ 6.0 (m, 1H, X of ABX, J_{AX} 16 Hz, J_{BX} 8 Hz), 4.2 (m, 2H, AB of ABX, J_{AB} 0) ppm.



$$Et_3SiCH{=}CH_2 + Me_3SiN_3 \rightarrow (Me_3Si)(Et_3Si)NCH{=}CH_2 \qquad \text{(II)}$$

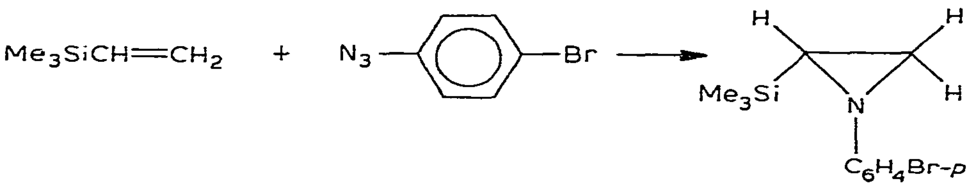
(II)

The product from higher reaction temperatures had a wider boiling range and a more complex spectrum in the vinyl region, attributable to the formation of both *N,N*-bis(trimethylsilyl)- and *N,N*-bis(triethylsilyl)-aminoethene arising from scrambling of the silyl groups between nitrogens.

No reaction occurred between vinyltrimethylsilane and trimethylsilyl azide under reflux but heating in hexane in a sealed tube at 130—140°C for 3 days led to 65% conversion to *N,N*-bis(trimethylsilyl)aminoethene, isolated by GLC (SE 30, 180°C) *m/e* 187 $(M)^+$, 172 $(M - \text{Me})^+$; IR: 6.25 μm (C=C); NMR: 0.18 (18H, s, Me_3Si), 6.10 (d of d, 1H, X of ABX, J_{AX} 16 Hz, J_{BX} 8Hz), 4.2, 4.14 (2d, each 1H, whose high field components overlap, J_{AB} 0) ppm.

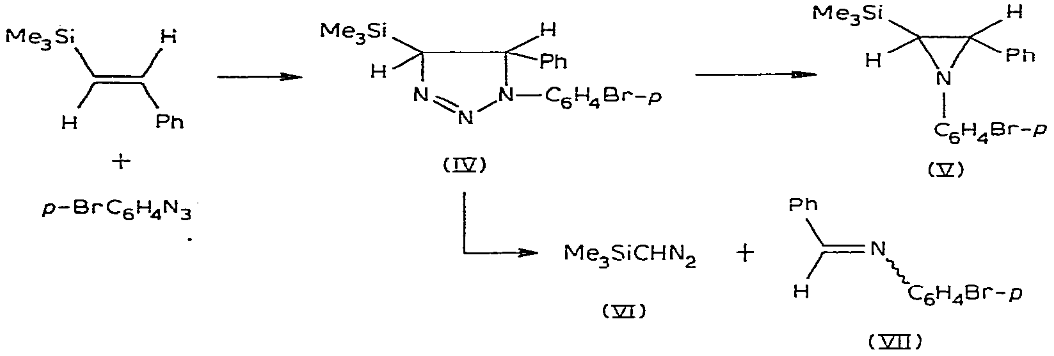
Only recovered starting materials were obtained from attempts to combine trimethylsilyl azide with vinyltriphenylsilane, or *trans*-triphenylsilylstyrene, arylsilanes apparently being less reactive.

Since phenyl azide and benzyl azide have been reported [3, 4], without accompanying spectral evidence, to react with vinylsilanes to give the corresponding aziridines, we investigated the reaction between *p*-bromophenylazide and vinyltrimethylsilane. After refluxing in CCl_4 for 48 h the reaction was virtually complete and the major product (55%) was the expected aziridine (III): b.p. (Kugelrohr oven temperature) 110—130°C/0.3 mmHg; NMR: δ 6.6—7.4 (4H, AB, aromatic), 2.0 (m, 2H, AB of ABX, J_{AX} 7.6 Hz, J_{BX} 4.6 Hz, J_{AB} 1.8 Hz), 1.2 (d of d, 1H, X of ABX) 0.1 (9H, s, Me_3Si) ppm; IR: no strong band at 6.2 μm.



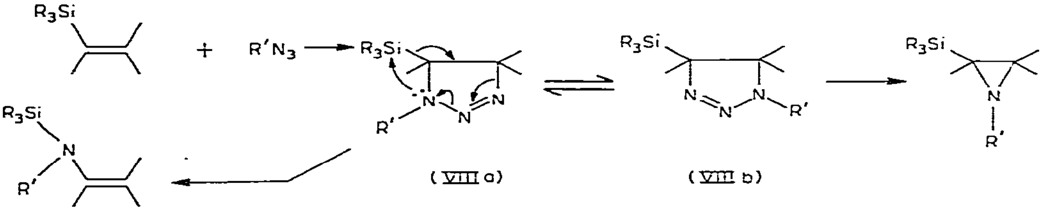
(III)

Similarly, the reaction of *p*-bromophenylazide and *trans*-trimethylsilylstyrene in refluxing CCl_4 was carried out. After 24 hours about 10% reaction had occurred, and new signals in the NMR (δ 4.1, 4.6 ppm, two doublets, *J* 7 Hz) were observed, probably attributable to the triazoline (IV).



After a total of 4 days heating, the signals due to IV had disappeared and signals due to the aziridine (V) (NMR: δ 2.1 (d, 1H, J 3 Hz, PhCH)), 1.7 (d, 1H, J 3 Hz, Me_3SiCH) ppm together with those of a 1/1 mixture of the retrocycloaddition product VI (δ 2.5, (s, CH) ppm; IR: 4.83 μm (CN_2) [8] and VII (δ 8.3, (s, CH=N) ppm) were observed.

We believe the formation of the bis(silyl)enamines is best explained as arising from appropriately substituted triazolines such as VIIIa (R′ = Me_3Si), since there is no evidence that the aziridines isolated (III, V) underwent any rearrangement to silylenamines. Triazoline VIIIa is probably the preferred cycloaddition product, based on electronic factors, and can lead directly to the bis(silyl)enamines as shown, but its isomer VIIIb may be the actual species formed, since cycloadditions are known to be very sensitive to steric influences.

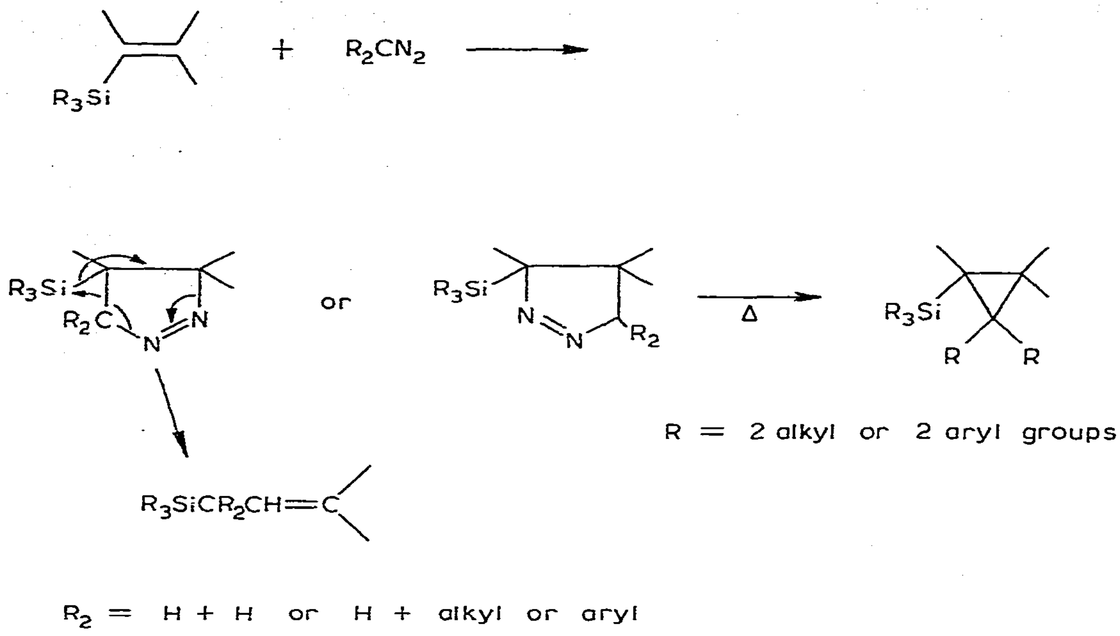


If VIIIb is the product of the cycloaddition (e.g. R = C_6H_4Br-p, as revealed by the retrocycloaddition products), thermolysis appears to lead only to loss of N_2 and formation of the aziridine. However, even if VIIIb were the regioisomer formed with silyl azides, its interconversion to VIIIa is possible, by way of a 1,3-N-to-N silyl migration as has been observed previously [5]*, so that in this case, regardless of regioselectivity, a bis(silyl)enamine can be formed.

This behaviour bears a close resemblance to that recently reported by Cunico [7] for reactions of vinylsilanes with diazoalkanes where an initially formed pyrazoline was observed, depending on regiochemistry, either to form a cyclopropane and nitrogen, or to undergo an analogous rearrangement involving bond formation between silicon and the adjacent ring carbon atom.

---

*Analogous 1,3-C-to-N silyl migrations have also been observed.



Acknowledgement

This work was supported by the National Research Council of Canada.

References

1 A.R. Bassindale, A.G. Brook, P. Chen, and J. Lennon, J. Organometal. Chem., 94 (1975) C21.
2 E. Ettenhuber and K. Rühlmann, Chem. Ber., 101 (1968) 743.
3 K.A. Andrianov, V.I. Sidorov and L.M. Khananashvili, Dokl. Akad. Nauk. SSSR 158, (1964) 987.
4 K.A. Andrianov, V.I. Sidorov and L.M. Khananashvili, J. Gen. Chem. USSR, 36 (1966) 178.
5 N. Wiberg and H.J. Pracht, Chem. Ber., 105 (1972) 1388.
6 A.R. Bassindale and A.G. Brook, Can. J. Chem., 52 (1974) 3474.
7 R.F. Cunico and H.M. Lee, J. Amer. Chem. Soc., 99 (1977) 7613.
8 D. Seyferth, H. Menzel, A.W. Dow and T.C. Flood, J. Organometal. Chem., 44 (1972) 279.