Tetrahedron Letters No. 48, pp 4681 - 4684. 0040-4039/79/1122-4681$02.00/0
©Pergamon Press Ltd. 1979. Printed in Great Britain.

CHLORINE BRIDGING IN RADICALS FROM 1-CHLORO-1,2,5-TRIMETHYL-1-SILACYCLOPENTANE

Peter R. Wells* and Fritz P. Franke

Department of Chemistry, University of Queensland, Brisbane 4067, Australia.

Summary: Radical chlorination in the 2-position of the isomers of 1-chloro-1,2,6-trimethyl-1-silacyclopentane displays a stereo-specificity consistent with the incursion of 1,2-chloro bridged intermediates.

When a mixture of the geometrical isomers of 1,2,5-trimethyl-1-silacyclopentane^1 is subjected to radical chain chlorination in carbon tetrachloride solution initiated by benzoyl peroxide a by-product of higher boiling point than the 1-chloro-1,2,5-trimethylsilacyclopentane is formed.^{2}

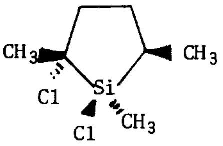
The by-product is obtained in *ca* 15% yield and can be collected at b.p. 100-104°/35 mm Hg. Its analysis, C, 43.0; H, 7.3; Cl, 34.5% (Calculated for $C_7H_{14}SiCl_2$ C; 42.6; H, 7.2; Cl, 36.0), and especially its mass spectrum, showing several sets of peaks corresponding to the isotopic distribution of 1:6:9 characterising dichloro-compounds, reveals it to be a dichlorotrimethylsilacyclopentane.

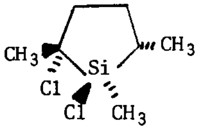
Gas chromatography (SE 30/S S.C.O.T. glass column) and PMR spectroscopy (100 MHz: $CDCl_3$ solution) show the by-product to be a mixture of two compounds, A and B, having retention times of 15.0 and 15.6 min. respectively (80°C; 80 mm Hg) and the PMR spectra given below (methyl groups only)

		A	B
Si-$\underline{CH}_3$	δ	0.62 singlet	0.65 singlet
C-$\underline{CH}_3$	δ	1.20 doublet (6.1 Hz)	1.08 doublet (6.3 Hz)
C-$\underline{CH}_3$	δ	1.70 singlet	1.68 singlet

These compounds are clearly two of the four possible enantiomeric pairs of 1,2-dichloro-1,2,5-trimethyl-1-silacyclopentanes (I-IV) below:-

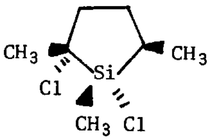
I
r-1, *t*-2, *c*-5

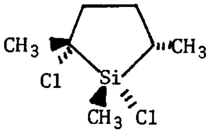




II
r-1, *t*-2, *t*-5

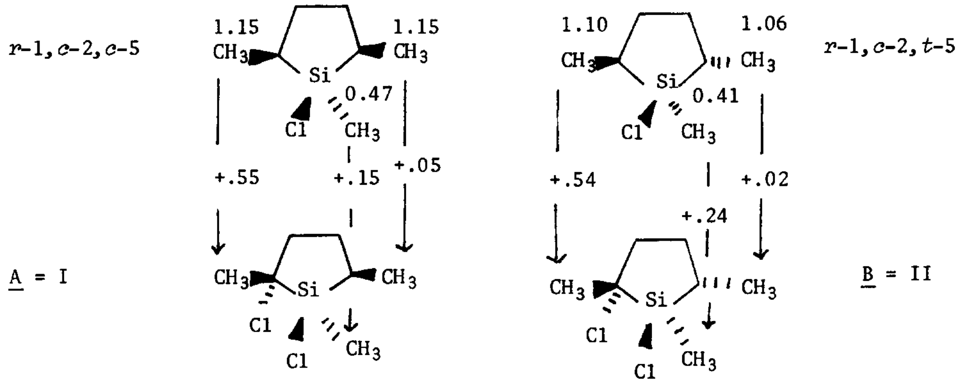
III
r-1, *c*-2, *c*-5



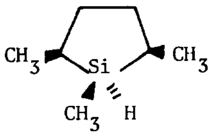


IV
r-1, *c*-2, *t*-5

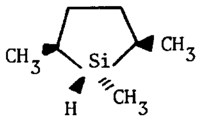
The singlet C_2-methyl groups in A and B are in essentially the same environments with respect to the major perturbing influences, i.e. the chloro-group, so that A and B must be either I and II or III and IV. Since the Si-methyl groups are substantially deshielded relative to their positions in the 1-chloro-derivatives,[2] they are most reasonably *cis* to the C_2-chloro group and hence A and B are I and II. Comparison with the corresponding 1-chloro-derivatives leads to the assignments of A as I; and B as II thus:-



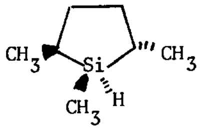
When essentially pure E,Z/Z,E-1,2,5-trimethyl-1-silacyclopentane (3), see figure below, is chlorinated a mixture of A (70%) and B (30%) is obtained, as by-product to the *r*-1,*c*-2,*t*-5-1-chloro-derivative. On the other hand the Z,Z- and E,E-1,2,5-trimethyl-1-silacyclopentanes (1 and 2) yield as by-products exclusively A and B respectively. The same pattern of products is observed when the appropriate chloro-derivative are subjected to further chlorination. Thus, unlike the monochlorination process and several other reactions in this system,[2] the stereochemical relationship between C_2 and C_5 is not maintained in the dichloro-compounds. There is however a high degree of stereo-specificity in the reaction and the two chloro-groups are found in *trans*-relationship.



(1)
ZZ
r-1,*c*-2,*c*-5

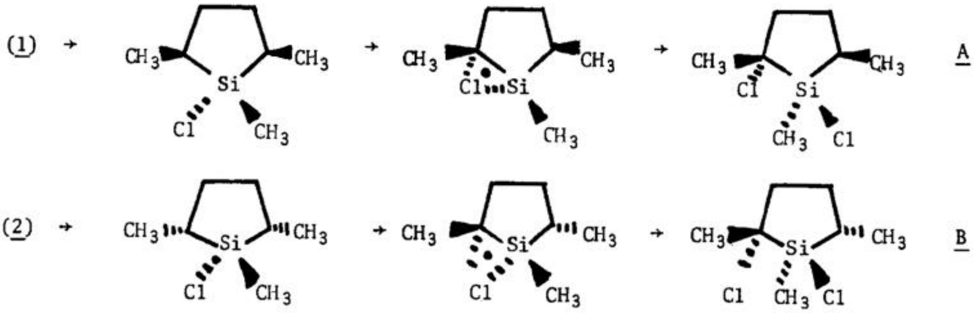


(2)
EE
r-1,*t*-2,*t*-5



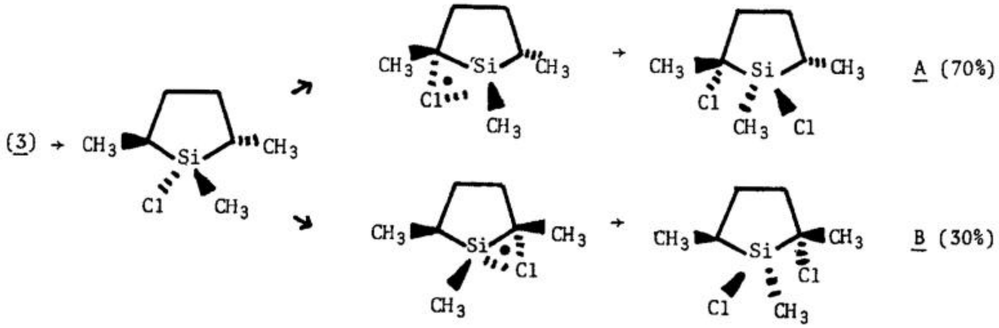
(3)
EZ/ZE
r-1,*c*-2,*t*-5

We consider these observations to be evidence of the incursion of radicals chloro-bridged between silicon and C_2 and suggest the following mechanism



in which the radical formed initially by hydrogen abstraction from C_2 (or equivalently C_5) is converted subsequently (or concurrently perhaps with anchimeric assistance) to the bridged radical. This then yields the dichloro-compound by reaction with CCl_4 at silicon from the opposite side to the bridge resulting in inversion of silicon. In the case of the ZZ-chloro-compound bridging must also invert C_2.

The formation of both products from the E,Z/Z,E-hydride arises from the two possible initial radicals



and it is noteworthy that where the bridging requires inversion of C_2 (i.e. in the reaction leading to B) the overall rate of reaction is not very much reduced (∿ 1/2). This implies that anchimeric assistance is not a significant feature.

Some of the conflicting evidence for and against bridged radicals has been reviewed by Huyser[3] who suggests that the phenomenon may be observed for radicals produced by the action of not-too reactive radicals and bearing bridging moieties with low energy, empty d-orbitals. In the present case the somewhat stabilised $Cl_3C\cdot$ radical initiates the process and chloro-groups are well known to undergo 1,2-shifts.

Bromination of 1,2,5-trimethyl-1-silacyclopentane with N-bromosuccinimide proceeds non-stereospecifically yielding approximately equal amounts of the E,E and Z,Z-1-bromo derivatives independently of the E,E/Z,Z content of the hydride employed. However, once again a higher boiling product is obtained containing only two 1,2-dibromo-derivatives arising from these and the EZ/ZE monobromo-derivatives. Comparisons of the ^1H and ^{13}C chemical shifts with those for the chloro-compounds shows that these are again most probably the *t*-2,*c*-5, and *t*-2,*t*-5 isomers. Thus, as would have been anticipitated, the bromo-group also engages in 1,2-bridging in this system.

On the other hand chlorination of 1-fluoro-1,2,5-trimethyl-1-silacyclopentane in carbon tetrachloride with benzoyl peroxide follows a distinctly different pattern indicating that the fluoro-group does not become involved. Initially the EE-isomer reacts to give a product which appears to *t*-1,*c*-2,*t*-5 2-chloro-1-fluoro-1,2,5-trimethyl-1-silacyclopentane, i.e. with retention at all centres, while the EZ/ZE-isomer yields two products in about 5:1 ratio, and the ZZ-isomer appears to react quite slowly. Ultimately a complex mixture of products is obtained. The EZ/ZE-isomer, for example, yields at least three major and four minor products indicating that in the absence of a bridging group radical attack can occur at several positions in the molecule.

REFERENCES

1. P.R. Wells and F. Franke, *J. Org. Chem.*, 44, 244 (1979).
2. F. Franke and P.R. Wells, *J. Org. Chem.*, in press.
3. E.S. Huyser in 'Organic Reactive Intermediates' Ed. by S.P. McManus, Academic Press Inc., N.Y. 1973, pp. 22-4; 44-6.

The authors thank Ing. H. Begutter and W. Deimbacher, Tobacco Research Institute, Vienna, for gc/ms analyses. Support of our work by the Australian Research Grants Committee is gratefully acknowledged.

(Received in UK 13 September 1979)