Journal of Organometallic Chemistry, 111 (1976) C21—C25

Preliminary communication

EVIDENCE FOR THE GENERATION OF A DISILACYCLOPROPANE IN SOLUTION

DIETMAR SEYFERTH* and DON P. DUNCAN

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received February 29th, 1976)

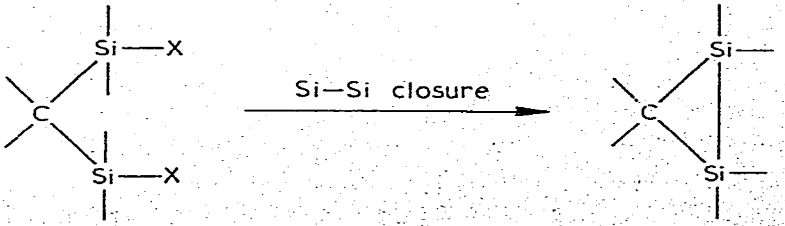
Summary

1,1,2,2-Tetramethyl-3-norcaranylidene-1,2-disilacyclopropane has been generated by the reaction of n-butyllithium with 1-chloro-2-(bromonorcaranyl)-tetramethyldisilane. Its reaction with methanol results in cleavage of the Si—Si bond.

In previous work we were able to prepare and characterize the first silacyclopropanes [1]. These highly strained compounds are exceptionally reactive when compared with silacarbocycles containing larger SiC_n rings, and in all reactions studied it was the polar Si—C bond which was broken by the attacking reagent. Disilacyclopropanes should be equally, if not more, reactive, but with many reagents we would expect the Si—Si linkage to be the one which is broken, rather than the Si—C bond.

Although disilacyclopropanes have been written as intermediates in organosilicon chemistry [2], no evidence concerning their possible existence has been presented to date. Indeed, we know of no published reports on their attempted preparation*.

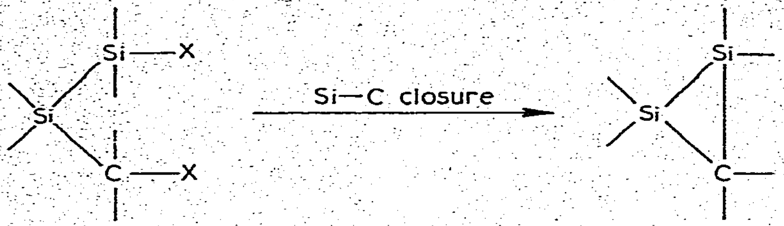
We report here some preliminary results on our investigation of the disilacyclopropane problem. A preparation of the disilacyclopropane ring system in principle could be effected in two ways:



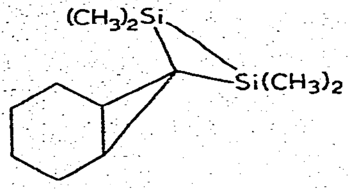
---

[*] A 1,2-disilacyclobutane [3] and several 1,2-disilacyclobutenes [4] have been reported. All are highly reactive, with the Si—Si bond being the site of reactivity.

or



The first method is simpler in terms of starting material preparation. However most reagents which might serve in the formation of the Si—Si bond to close the CSi_2 ring would also be expected to attack the Si—Si linkage and open the ring again. For this reason we chose to investigate the second procedure. Spiroannelated cyclopropane rings can play a decisive role in stabilizing the silacyclopropane ring [5] and therefore the target disilacyclopropane structure chosen was one containing this feature (I).



(I)

The route used in the preparation of I is shown in Scheme 1. The initial reaction was carried out under nitrogen in a pair of 200 ml three-necked, round-bottom flasks equipped with paddle stirrers which were connected via a glass tube containing a Teflon stopcock (Fig. 1). Flask B was charged with 20 ml of dimethyl ether (cooling to −90°C with liquid nitrogen), 60 ml of dry THF and 65.6 mmol of 7,7-dibromonorcarane, flask A with 50 ml of dimethyl ether and 73.7 mmol of 1,2-dichlorotetramethyldisilane [6].

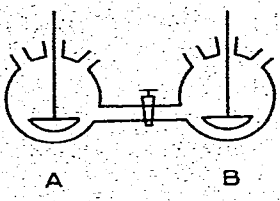
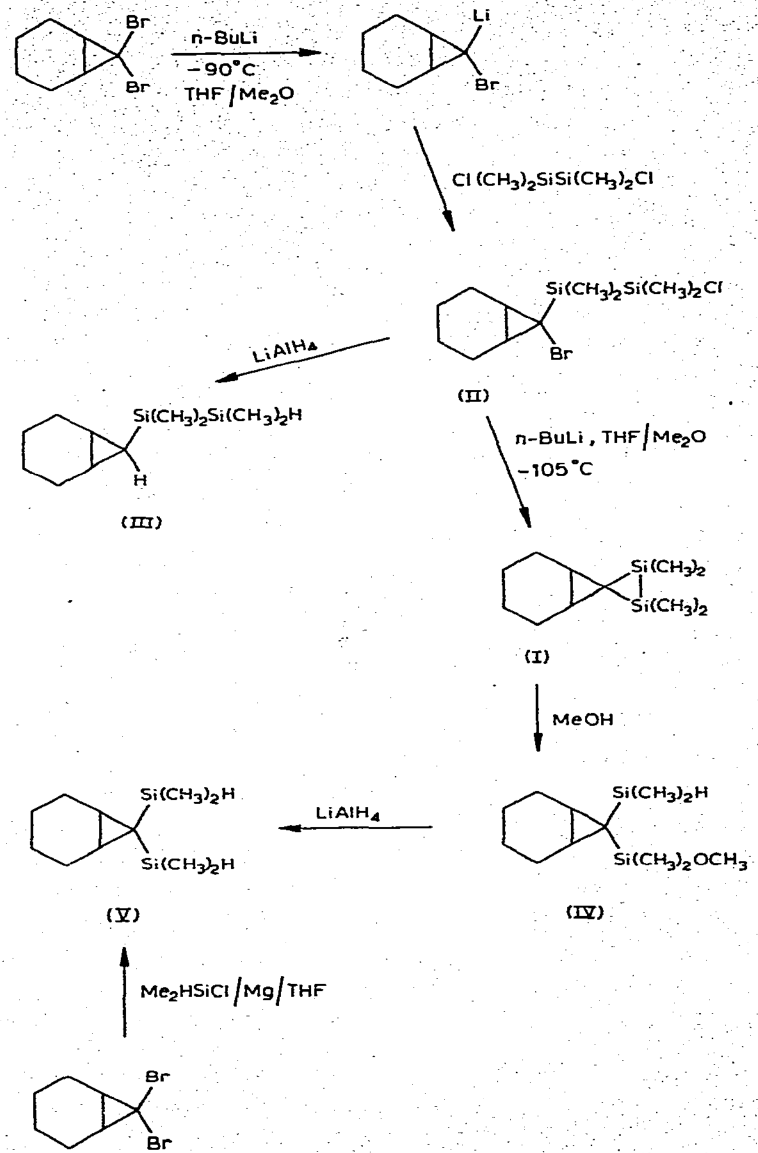


Fig.1.

n-Butyllithium in hexane (70 mmol) then was added slowly to flask B, with stirring, in order to prepare 7-bromo-7-lithionorcarane [7]. When preparation of this reagent was complete, the stopcock was opened and the yellow reagent solution was transferred by nitrogen pressure to flask A where its reaction with $ClMe_2SiSiMe_2Cl$ could take place. The reaction mixture was stirred at −90°C for 30 min to give a clear solution containing a white precipitate of lithium halide.

SCHEME 1

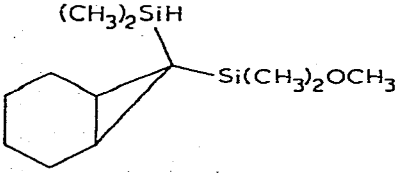


Treatment of the crude product obtained in such a preparation after filtration and solvent removal with lithium aluminum hydride in diethyl ether gave III in 37% yield. The NMR spectrum of this product (in CCl_4) supported the assigned structure: δ 3.69 (m, 1H, Si—H), 2.09—1.04 (m, 10H), 0.22 (s, 6H, $Si\underline{Me_2}SiMe_2H$), 0.15 (d, J 3.8 Hz, 6H, $Si\underline{Me_2}H$) and −0.30 ppm (t, J 9.1 Hz, cyclopropane H). The Si—H stretching vibration (in CCl_4) was observed at 2092 cm^{-1}. Reduction of Si—Cl linkages with $LiAlH_4$ is a well-known reaction and the reduction of cyclopropyl halides with this reagent also is known [8]. The presence of the desired intermediate II having been established, the ring closure reaction could now be studied.

The reaction mixture from the above 65.6 mmol preparation of II was transferred to a larger flask (under nitrogen) and diluted with 500 ml of THF and 500 ml of dimethyl ether. The resulting solution was cooled to —105°C and 65 mmol of n-butyllithium in hexane was added very slowly. The reaction mixture was stirred at —105°C for 1 h, allowed to warm to —25°C and treated with 40 ml of anhydrous methanol. Work-up of the mixture thus obtained, followed by GLC examination of the higher boiling components showed the presence of IV as the main product in about 10% yield based on the n-butyllithium used in the preparation of II. The methanolysis product provides good evidence that I had been formed; the silacyclopropane ring is very easily opened by reaction with methanol [1]. The NMR spectrum of IV was compatible with its assigned structure: δ 4.01 (m, 1H, Si—H), 3.31 (s, 3H, OMe), 2.09—0.99 (m, 10H), 0.15 (d, J 4.0 Hz, 6H, $\mathrm{Si\underline{Me}_2H}$) and 0.06 ppm (s, 6H, $\mathrm{Si\underline{Me}_2SiMe_2H}$). Further proof of the structure of IV was provided by means of its $\mathrm{LiAlH_4}$ reduction to V, an authentic comparison sample of which was prepared via Barbier-type dimethylhydrosilylation of 7,7-dibromonorcarane [9]. NMR of V: δ 4.12 (m, 1H, Si—H), 3.59 (m, 1H, Si—H), 2.11—0.91 (m, 10H) and 0.21 ppm (d, J 4.5 Hz, 6H, $\mathrm{Me_2Si}$).

This sequence of reactions provides strong evidence that the disilacyclopropane I had indeed been formed as shown in Scheme 1. Attempts to isolate I have not been successful, and it does not appear to survive intact when the reaction mixture is allowed to warm to room temperature. Whether I is thermally unstable or whether it is destroyed by reaction with some other component in the reaction mixture is not known.

As expected, it is the Si—Si bond, not the Si—C linkage, of the disilacyclopropane which is cleaved by methanol. It is interesting to note that the reaction of I with methanol appears to be stereospecific. According to the GLC behavior and the NMR spectrum of the methanolysis product IV, only one of the two possible isomers was formed. Since the *anti*-dimethylsilylene group of I is less hindered, we suggest that the isomer of IV which is obtained is the one which has the dimethylmethoxysilyl group in the *anti* position and the dimethylhydrosilyl group in the *syn* position (VI).



(VI)

All new compounds isolated in this study have been characterized by means of their spectroscopic properties; satisfactory combustion analyses have been obtained for all. We are continuing our studies in this area.

Acknowledgment

The authors are grateful to the Air Force Office of Scientific Research (NC)-AFSC (Grant AFOSR-76-2917), for generous support of this work.

References

1 (a) R.L. Lambert, Jr. and D. Seyferth, J. Amer. Chem. Soc., 94 (1972) 9246; (b) D. Seyferth, C.K. Haas and D.C. Annarelli, J. Organometal. Chem., 56 (1973) C7; (c) D. Seyferth and D.C. Annarelli, J. Amer. Chem. Soc., 97 (1975) 2273; (d) D. Seyferth, J. Organometal. Chem., 100 (1975) 237.
2 D.N. Roark and G.J.D. Peddle, J. Amer. Chem. Soc., 94 (1972) 5837.
3 J.C. Thompson, J.L. Margrave and P.L. Timms, Chem. Commun., (1966) 566.
4 (a) C.S. Liu, J.L. Margrave, S.C. Thompson and P.L. Timms, Can. J. Chem., 50 (1972) 459; (b) C.S. Liu, J.L. Margrave and J.C. Thompson, Can. J. Chem., 50 (1972) 465; (c) C.S. Liu and J.C. Thompson, Inorg. Chem., 10 (1971) 1100; (d) W.H. Atwell and J.G. Uhlmann, J. Organometal. Chem., 52 (1973) C21.
5 P.D. Mollere and R. Hoffmann, J. Amer. Chem. Soc., 97 (1975) 3680.
6 M. Ishikawa, M. Kumada and H. Sakurai, J. Organometal. Chem., 23 (1970) 63.
7 D. Seyferth, R.L. Lambert, Jr. and M. Massol, J. Organometal. Chem., 88 (1975) 255.
8 C.W. Jefford, D. Kirkpatrick and F. Delay, J. Amer. Chem. Soc., 94 (1972) 8905.
9 D. Seyferth and R.L. Lambert, Jr., J. Organometal. Chem., 88 (1975) 287.