Journal of Organometallic Chemistry, 70 (1974) C3—C4

Preliminary communication

SYNTHESIS OF 3,4-BENZO-1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOPENTENE

F.P. TSUI* and G. ZON

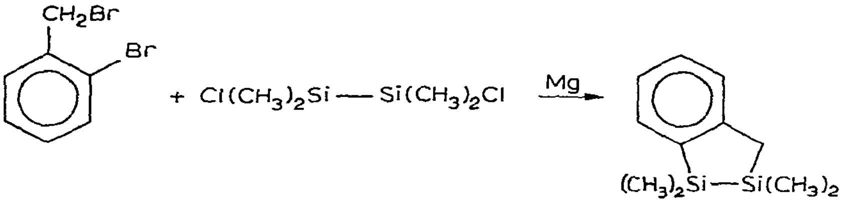
Maloney Chemical Laboratory, The Catholic University of America, Washington, D.C. (U.S.A.)

(Received February 5th, 1974)

Summary

Magnesium coupling of 1,2-dichlorotetramethyldisilane and *o*-bromobenzyl bromide has been found to readily afford 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclopentene. This new ring system undergoes facile oxidation to its corresponding disiloxane.

Current procedures for preparing 1,2-disilacyclopentane derivatives involve silicon—silicon bond formation via reductive [1, 2] or pyrolytic [3] intramolecular cyclization of chlorosilyl functionalities. We now report that 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclopentene (I), which is a new ring system, can be conveniently synthesized in moderate yield by intermolecular cyclization of *o*-bromobenzyl bromide and 1,2-dichlorotetramethyldisilane [4] with magnesium. An analogous reaction using dichlorodimethylsilane has been previously reported [5] for the preparation of 2,3-benzo-1,1-dimethylsilacyclobutene.



(I)

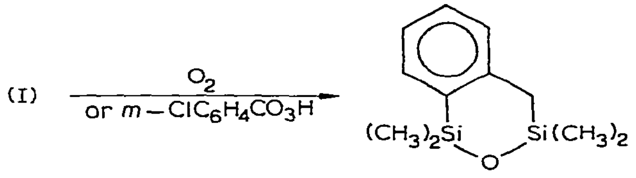
The method simply involves slow addition (4 h) of the dibromide (25 mmole) and dichloride (25 mmole) in ether (20 ml) to a refluxing suspension of magnesium turnings (75 mmole) in ether (5 ml). Additional reflux (1 h) was

---

[*] PRF-ACS Undergraduate Research Participant, 1973—1974.

followed by conventional ammonium chloride hydrolysis and work-up, and gave a 44% yield (GLC) of (I), b.p. 70° (1 mm), δ(CCl_4, TMS) (60 MHz) 7.60—6.97 (m, 4), 2.27 (s, 2), 0.30 (s, 6) and 0.22 (s, 6)*.

Analytically pure samples of (I) require ultimate purification by GLC (15% Apiezon), due to the expected [2, 7] susceptibility of this strained system toward air oxidation and formation of disiloxane (II), δ(CCl_4, TMS) (60 MHz) 7.53—6.98 (m, 4), 2.14 (s, 2), 0.31 (s, 6), 0.09 (s, 6); ν(SiOSi) 968 cm^{-1}. A semi-quantitative indication of the enhanced oxidative reactivity for (I) follows from



(II)

competitive oxidation [8] of (I) (1 equiv.) and pentamethylphenyldisilane (III) (1 equiv.) with *m*-chloroperbenzoic acid (1 equiv.) in dichloromethane, wherein quantitative conversion of (I) to (II) was effected with ⩽ 5% oxidation of (III) to its corresponding disiloxane.

Extension of the present method to the synthesis of more highly strained 1,2-disilacyclobutene [9] and disilacyclopropane derivatives is in progress.

Acknowledgements

Partial financial support of this research by the donors of The Petroleum Research Fund, administered by the ACS, and The Catholic University of America is gratefully acknowledged.

References

1 H.A. Clark, U.S. Patent 2,563,004, 1949; Chem. Abstr., 45 (1951) 10676.
2 M. Kumada, K. Tamao, T. Takubo and M. Ishikawa, J. Organometal. Chem., 9 (1967) 43.
3 E.A. Chermyshev, N.B. Komalenkova, T.A. Klochkova, S.A. Shchepinov and A.M. Mosin, Zh. Obshch. Khim., 41 (1971) 122.
4 H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, Tetrahedron Lett., (1966) 5493.
5 C. Eaborn, D.R.M. Walton and M. Chan, J. Organometal. Chem., 9 (1967) 251; see also K. Tamao, M. Kumada and M. Ishikawa, ibid., 31 (1971) 17; L. Birkofer and W. Weniger, Chem. Ber., 106 (1973) 3595.
6 R. Calas, A. Marchand, E. Frainnet and P. Gerval, Bull. Soc. Chim. Fr., (1968) 2478.
7 V.Yu. Orlov, L.E. Gusel'nikov, N.S. Nametkin and R.L. Ushakova, Org. Mass Spec., 6 (1972) 309.
8 K. Tamao and M. Kumada, J. Organometal. Chem., 31 (1971) 35.
9 C.S. Liu, J.L. Margrave, J.C. Thompson and P.L. Timms, Can. J. Chem., 50 (1972) 459; C.S. Liu, J.L. Margrave and J.C. Thompson, ibid., 50 (1972) 465; W.H. Atwell and J.G. Uhlmann, J. Organometal. Chem., 52 (1973) C21.

---

*Assignment of a ten-membered ring dimeric structure for (I) was excluded on the basis of its boiling point [cf. pentamethylphenyldisilane, lit. [6] b.p. 113—115° (25 mm)], mass spectrum, and chemical conversion to disiloxane (II) (vide infra) with one equivalent of *m*-chloroperbenzoic acid.