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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.)

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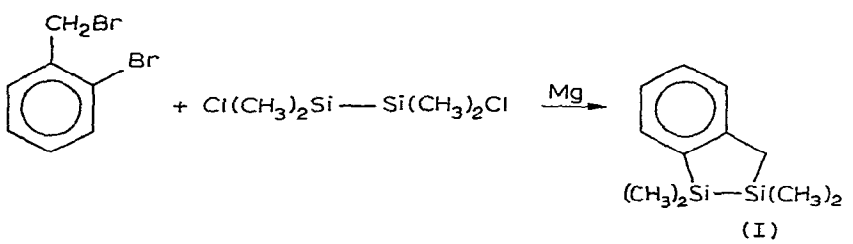
Summary

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.



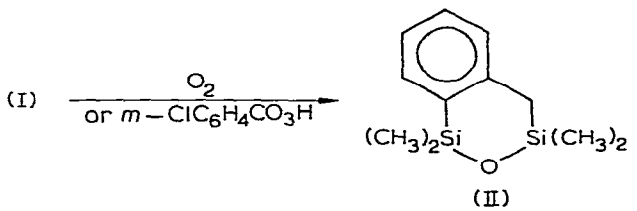
(I)

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

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*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.