Tetrahedron Letters,Vol.26,No.24,pp 2837-2840,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

TOWARDS TETRASILABICYCLO[1.1.0]BUTANE: REDUCTIVE COUPLING OF 1-t-BUTYL-2,2-DIMESITYL-1,1,2-TRICHLORODISILANE[1]

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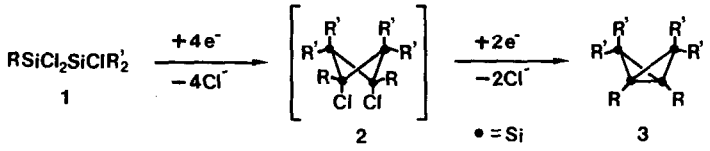
Abstract: Reductive coupling of 1-t-butyl-2,2-dimesityl-1,1,2-trichlorodisilane employing Li-naphthalenide furnishes, on oxygenation or hydrolysis of the reaction mixture, products (8-11) that may arise from insertion of oxygen into or the addition of water across the Si-Si bonds of 1,3-di-t-butyl-2,2,4,4-tetramesityltetrasilabicyclo-[1.1.0]butane (3).

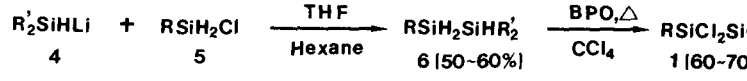
The preparation of bicyclic polysilanes has received limited attention despite considerable interest in the properties of these compounds and cyclic polysilanes in general.[2] This is due, in part, to the dearth of general synthetic methods for the regioselective formation of silicon-silicon bonds that are required for their construction.

We report here an initial attempt to prepare the lowest homologue of this family of compounds, tetrasilabicyclo[1.1.0]butane, by reductive coupling of a 1,1,2-trichlorodisilane. The reductive dimerization of symmetrical 1,2-dichlorodisilanes has been reported and provides symmetrical cyclotetrasilanes in variable yields.[3] We envisaged that a trichlorodisilane (1) with a suitable combination of substituents R and R' might couple in a regioselective fashion to provide an intermediate 1,3-dichlorocyclotetrasilane (2) that would undergo subsequent ring closure to form the bicyclic compound 3 (eqn. 1).



(eqn. 1)

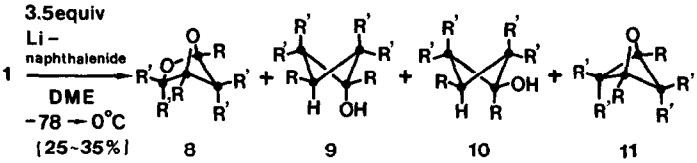
In practice, we chose 1-t-butyl-2,2-dimesityl-1,1,2-trichlorodisilane (1, R=t-butyl, R'=mesityl) as a possible precursor for compound 3. The synthesis of trichlorodisilane 1 was executed as follows: Dimesitylsilyllithium (4), prepared from dimesitylchlorosilane[4] (4.67 g, 15.4 mmol) and Li dispersion (1% Na, 0.42 g, 60.5 mg atoms) in THF (45 mL) at 0°C, was added dropwise to a solution of t-butylchlorosilane (5)[5] (1.99 g, 16.2



(eqn. 2)

mmol) in hexane (100 mL) at -78°C. After warming to room temperature, aqueous workup followed by flash chromatography provided 1-t-butyl-2,2-dimesityldisilane (6)[5] in 50-60% yield (eqn. 2). Chlorination of compound 6 was achieved by the addition of dibenzoyl peroxide (150 mg, 0.6 mmol) in CCl_4 (15 mL) to a refluxing solution of 6 (1.2 g, 3.4 mmol) and dibenzoyl peroxide (25 mg, 0.1 mmol) in CCl_4 (15 mL) over 48-72 h by syringe. Kugelrohr distillation of the mixture furnished trichlorodisilane 1[5] in 60-70% yield.

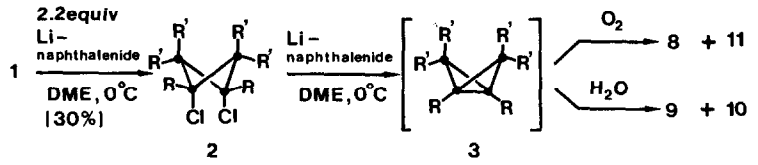
Reductive Coupling of Compound 1: Addition of trichlorodisilane 1 (500 mg, 1.09 mmol) dissolved in DME (3 mL) to lithium naphthalenide, [prepared by sonication of lithium (26.5 mg, 3.82 mmol) and naphthalene (490 mg, 3.82 mmol) in DME (3 mL) at 0°C for 2 h], at -78°C followed by warming the mixture to 0°C provided a pale red mixture after about 1 h at 0°C . Addition of hexane (6 mL) and filtration through Celite, followed by removal of solvent in vacuo provided a pale yellow solid residue. Flash chromatography on silica gel eluting with hexane:benzene 5:1 to 1:1 provided four cyclic compounds, in order of decreasing R_f, identified as 1,4-di-t-butyl-3,3,5,5-tetramesityl-2,6-dioxa-1,3,4,5-tetrasilabicyclo[2.1.1]hexane (8),[6] cis-1,3-di-t-butyl-1-hydroxy-2,2,4,4-tetramesitylcyclotetrasilane (9),[7] trans-1,3-di-t-butyl-1-hydroxy-2,2,4,4-tetramesitylcyclotetrasilane (10)[8] and 1,3-di-t-butyl-2,2,4,4-tetramesityl-5-oxa-1,2,3,4-tetrasilabicyclo[1.1.1]pentane (11)[9] in a combined yield of 25-35%[10] in addition to polymeric material (eqn. 3). (See below for the structural assignments).



(eqn. 3)

Compounds 8 and 11 could be prepared in 20-25 and 10-15% yield, respectively, to the exclusion of silanols 9 and 10 if the whole reaction mixture was separated from residual lithium and dry oxygen was passed through the pale red mixture (see above) for several minutes. Alternately, if the mixture was cannulated into a vortex of degassed pH 7 phosphate buffer under argon only compounds 9 and 10 were isolated in 25-30 and 5-10% yield, respectively.

If trichlorodisilane 1 (740 mg, 1.61 mmol) in DME (3 mL) was treated dropwise with 4 mL of a solution of lithium naphthalenide in DME (0.89 M, 2.2 equiv.) at 0°C and the resulting pale yellow mixture cannulated into a vortex of ice-cold pH 7 buffer, cis-1,3-di-t-butyl-1,3-dichloro-2,2,4,4-tetramesitylcyclotetrasilane (2)[11] can be isolated in 30% yield (eqn. 4). Under these conditions compounds 8-11 are not present in significant amounts. Compound 2 can also be isolated in 20-25% yield under the conditions used to prepare compounds 8-11 (vide supra) if the reaction mixture is quenched into pH 7 buffer



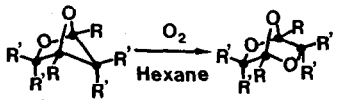
(eqn. 4)

several minutes after the solution has reached 0°C. These results indicate that dichlorocyclotetrasilane 2 is a possible precursor to compounds 8-11.

An explanation that accounts for the formation of compounds 8-11 involves the intermediacy of 1,3-di-t-butyl-2,2,4,4-tetramesityltetrasilabicyclo[1.1.0]butane (3, R=t-butyl, R'=mesityl), formed by reductive coupling of dichlorocyclotetrasilane 2, which is converted to compounds 11 and 8 by successive oxygen insertions or forms silanols 9 and 10 by the addition of water across the central Si-Si bond (eqn. 4).[12] An ^{1}H-NMR spectrum of the reaction mixture, obtained with strict exclusion of water and oxygen, reveals that none of these compounds are present prior to workup. However, the complexity of the mixture does not permit unambiguous identification of compound 3 and thus alternative explanations that could account for the formation of products 8-11 cannot, at present, be rejected.

The structures of compounds 8 and 11 (and silanols 9 and 10) were established by by variable temperature ^{1}H-NMR spectroscopy in conjunction with mass spectrometry. At low temperature (-48°C), twelve distinct singlets of equal intensity assigned to the o- and p-methyl protons on the mesityl rings of compound 8[6] were observed. In addition, two signals assigned to non-equivalent t-butyl groups were present. At high temperature (100°C), six signals of equal intensity were observed for the o- and p-methyl groups and two signals for the t-butyl protons. Evidently, rapid rotation of each of the four non-equivalent aryl rings at high temperature renders the o-methyl groups on each ring equivalent giving rise to four signals. The remaining two signals, assigned to the p-methyl protons indicate accidental chemical shift equivalence at this temperature. Thus, compound 8 posesses C_1 symmetry. In contrast, the ^{1}H-NMR spectrum of compound 11[9] at -78°C exhibited only five signals, assigned to the o- and p-methyl protons, in a ratio of 1:1:2:1:1 and one t-butyl resonance. At 100°C, two of the former signals had coalesced and four signals were observed (ratio 2:1:2:1) in addition to the single t-butyl resonance. These data support the conclusion that compound 11 has C_2 symmetry at low temperatures, but at high temperature has time-averaged C_{2v} symmetry with two aryl rings undergoing rapid rotation along the Si-C bond such that four o-methyl groups become equivalent. The strong molecular ions observed at m/e 734 and 718 in the mass spectra of compounds 8 and 11, respectively confirm the assigned structures.

Compound 8 was unstable with respect to further oxygenation in solution and deposited single crystals of 1,4-di-t-butyl-3,3,6,6-tetramesityl-2,5,7-trioxa-1,3,4,6-tetrasilabicyclo[2.2.1]heptane (12) after standing several days in hexane (eqn. 5). The crystal structure of compound 12, to be published elsewhere, provides further confirmation of the structure of compound 8.



8 12 (eqn. 5)

In conclusion, we have presented indirect evidence for the existence of tetrasilabicyclo[1.1.0]butane 3 prepared by reductive coupling of trichlorodisilane 1. Even with

the bulky substituents present, species 3 shows unexpectedly high reactivity towards oxygen and water. The synthesis and coupling of more sterically hindered trichlorodisilanes is obviously required and will be reported in due course.

References and Footnotes

1. S.C.: Natural Sciences and Engineering Research Council NATO Postdoctoral Fellow. J. A. D. and S. Murakami: on leave from Lewis & Clark College, Oregon and Yoshitomi Ind, respectively. Financial Support: The National Science Foundation, U.S.A., Yoshitomi Industries Ltd., and Kao Corporation, Japan. High resolution mass spectra: NIH Grant PR00317 (principal investigator, Professor K. Biemann).
2. a) Boudjouk, P.; Sooriyakumaran, R., J. Chem. Soc. Chem. Commun., 1984, 777. b) Stallings, W.; Donohue, J., Inorg. Chem., 1976, 15, 524. c) Kumada, M., J. Organomet. Chem., 1975, 100, 127. d) West, R.; Carberry, E. Science, 1975, 189, 179. e) West, R.; Indriksons, A., J. Am. Chem. Soc., 1972, 94, 6110.
3. Watanabe, H.; Inose, J., Fukushima, K.; Kougo, Y.; Nagai, Y., Chem. Lett., 1983, 1711.
4. Lapkin, I.I.; Rogozhnikova, I.S.; Zhukov, M.A., Zh. Obshch. Khim., 1973, 43, 1739.
5. Compounds 1, 5 and 6 were identified by their IR, ^{1}H-NMR and mass spectra. Full details for their preparation are available from the authors by request.
6. Compound 8: mp 260-265°C; IR ($CHCl_3$) 3035, 2960, 2925, 2890, 2835, 1603, 1458, 1405, 1019, 850 cm^{-1}; ^{1}H-NMR (250 MHz, Toluene-d_8, -48°C) δ 6.79(br s, 2H), 6.63(s, 1 H) 6.51(s, 2H), 6.47(s, 1H), 6.27(s, 1H), 6.10(s, 1H), 3.00(s, 3H), 2.86(s, 3H), 2.76 (s, 3H), 2.50(s, 3H), 2.32(s, 3H), 2.30(s, 3H), 2.20(s, 3H), 2.15(s, 3H), 2.11(s,3H), 2.07(s, 3H), 2.05(s, 3H), 2.02(s, 3H), 1.41(s, 9H), 1.19(s, 9H); (100°C) δ 6.69(s, 2H), 6.68(s, 1H), 6.64(s, 2H), 6.5-6.2(br s, 2H), 6.10(s, 1H), 2.50(s, 6H), 2.45(s, 6H), 2.22(s, 6H), 2.14(s, 6H), 2.08(s, 6H), 2.01(s, 6H), 1.33(s, 9H), 1.10(s, 9H); Mass spectrum calculated for $C_{44}H_{62}O_2Si_4$: 734; Found (EI): 734.
7. Compound 9: mp 203-206°C; IR (Nujol) 3585, 3025, 2091, 1603, 1472, 1438, 1404, 1022, 845, 757, 668 cm^{-1}; ^{1}H-NMR (250 MHz, Toluene-d_8, 0°C) δ 6.86(s, 2H), 6.72(s, 2H), 6.68(s, 2H), 6.59(s, 2H), 4.74(s, 1H), 2.61(s. 6H), 2.55(s, 6H), 2.50(s, 6H), 2.28 (s, 6H), 2.15(s, 12H), 1.71(s, 1H), 1.18(s, 9H), 1.12(s, 9H); (100°C) δ 6.74(s, 4H),6.72(s, 4H), 4.67(s, 1H), 2.48(s, 12H), 2.38(s, 12H), 2.13(s, 6H), 2.11(s, 6H), 1.57(s, 1H), 1.11(s, 9H), 1.06(s, 9H); High resolution mass spectrum calculated for $C_{44}H_{64}OSi_4$: 720.403; Found (EI): 720.403. The assigned stereochemistry is very likely correct, but has not been established.
8. Compound 10: mp, 273-282°C; IR (Nujol) 3460, 2095, 1600, 1463, 1452, 1008, 943, 802, 775, 756 cm^{-1}; ^{1}H-NMR (250 MHz, Tolune-d_8, 100°C) δ 6.73(s, 4H), 6.69(s, 4H), 4.88 (s, 1H), 2.53(br s, 6H), 2.35(s, 6H), 2.11(s 6H), 2.10(s, 6H), 2.09(s, 6H), 2.08 (s, 6H), 1.57(s, 1H), 1.06(s, 9H), 1.03(s, 9H); mass spectrum calculated for $C_{44}H_{64}OSi_4$ 720.403; Found (EI): 720.402. The assigned stereochemistry is very likely correct, but has not been established.
9. Compound 11: mp 222-226°C; IR ($CHCl_3$) 3050, 2950, 2915, 2825, 1595, 1444, 1190, 1010, 839 cm^{-1}; ^{1}H-NMR (250 MHz, Toluene-d_8, -78°C) δ 6.83(s, 2H), 6.54(s, 2H), 6.50(s, 2H), 6.48(s, 2H), 3.06(s, 6H), 2.37(s, 6H), 2.16(s, 12H), 2.01(s, 6H), 1.95(s, 6H), 1.36(s, 18H); (100°C) δ 6.71(s, 4H), 6.51(s, 4H), 2.53(s, 12H), 2.17(s, 6H), 2.15(s, 12H), 2.08(s, 6H), 1.29(s, 18H); High resolution mass spectrum calculated for $C_{44}H_{62}OSi_4$: 718.388; Found (EI): 718.386
10. The relative amounts of compounds 8-11 can vary considerably if the mixture is exposed to the atmosphere.
11. Compound 2: mp > 300°C; IR($CHCl_3$) 3040, 2950, 2915, 2850, 1598, 1445, 1282, 1254, 1000, 843 cm^{-1}; ^{1}H-NMR(250 MHz, Toluene-d_8, 12°C) δ 6.85(s,1.2H), 6.82(s, 1.2H), 6.75 (s, 1.6H), 6.62(s, 0.8H), 6.49(s, 0.8H), 6.45(s, 2.4H), 3.09(s, 3.6H), 2.82(s, 2.4H), 2.76(s, 2.4H), 2.28(s, 2.4H), 2.21(s, 7.2H), 2.10(s, 4.8H), 2.05(s, 3.6H), 1.98(s,3.6 H), 1.27(s, 10.8H), 0.84(s, 7.2H);(100°C) δ 6.75-6.54(br d, 8H), 2.8-2.2(br d, 24H), 2.05(s, 12H), 1.15 (br s, 18H); mass spectrum (EI): 772 (M^+,$^{35}Cl_2$).
12. Insertion of oxygen into or addition of water (or alcohols) to strained Si-Si or Si-C bonds is facile. a) Fritz, V.G.; Wartanessian, S.; Maun, E.; Honle, W.; Schnering, H.G.v., Z. Anorg. Allg. Chem., 1981, 475, 87. b) Sakurai, H.; Kobayashi, T.; Nakadaira, Y., J. Organomet. Chem., 1978, 162, C 43. c) Seyferth, D. J. Organomet. Chem, 1975, 100, 237.

(Received in USA 8 January 1985)