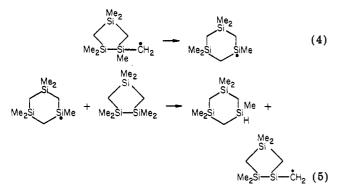
lecularly to  $Me_3SiCH_2SiMe_2$ . The corresponding reaction in this case, followed by hydrogen abstraction, would give PTSH (eq 4 and 5). Reactions 4 and 5 constitute the propagation steps of a chain reaction converting HTSP to PTSH.



In the pyrolysis of HTSP at higher pressure,<sup>1</sup> the radical formed in reaction 1 would react mainly by reaction 3 instead of by reaction 2, thus initiating the chain leading to PTSH. Termination of the chain would probably be by self-combination of



reaction 6, giving three-halves-order kinetics,<sup>6</sup> with  $k_{3/2} = (k_1k_5^2/2k_6)^{1/2}$ . From the present work and by analogy with the isomerization of hexamethyldisilane,<sup>7</sup> Arrhenius parameters may be estimated for these reactions, as shown in the Table I. Hence, for  $k_{3/2}$ ,  $\log_{10} A = 13.9$  and E/kJ mol<sup>-1</sup> = 233.

For the isomerization of HTSP to PTSH, the chain length  $\lambda$  is given by  $\lambda = k_{3/2} (\text{HTSP})^{1/2}/k_1$ . Under the

original conditions,<sup>1</sup> the pressure was at least 1 atm and a typical temperature was 773 K. These conditions give a chain length of ca. 400, thus explaining the preponderant formation of PTSH. In contrast, the chain length under LPP conditions is only 0.4 at 939 K, diminishing to 0.2 at 1036 K. In fact, termination in the LPP apparatus is unlikely to be by the bimolecular reaction (6) but is more likely to be by unimolecular loss of the same radical to the walls of the reaction vessel. The formation of PTSH would then be second order, with even shorter chain lengths than those calculated above, resulting in the formation of TDSB by reaction 2 instead. Reactions 1–6 thus provide a satisfactory explanation for the different course of the pyrolysis of HTSP at high and low pressure.

The radical rearrangement (4) is exothermic by at least<sup>17</sup> 30 kJ mol<sup>-1</sup>; from this work and from that on hexamethyldisilane<sup>6</sup> it appears to be rather a general reaction of alkyl silanes containing silicon-silicon bonds and is probably important in the pyrolytic formation of siliconcarbon fibers.

#### **Experimental Section**

HTSP and PTSH were prepared as previously described,<sup>1</sup> and TDSB was prepared by pyrolysis of 1,1-dimethyl-1-silacyclobutane<sup>13</sup> followed by purification by preparative GLC.

The LPP apparatus<sup>2</sup> was modified by addition of a dedicated microcomputer with real-time clock (RML 380Z), which received peak height measurements and times from an eight-channel peak selector, and was used for processing the kinetic results directly.

Acknowledgment. I.M.T.D. and F.T.L. thank the Science and Engineering Research Council for financial support.

**Registry No.** HTSP, 58679-67-7; PTSH, 17882-80-3; TDSB, 1627-98-1; Me<sub>2</sub>Si, 6376-86-9; Me<sub>2</sub>Si=CH<sub>2</sub>, 4112-23-6; HCl, 7647-01-0; methyl trimethylsilyl ether, 1825-61-2; pentamethylchlorodisilane, 1560-28-7; 1,1-dimethyl-1-silacyclobutane, 2295-12-7; dimethyl-mercury, 593-74-8; methyl, 2229-07-4.

# Pyrolytic Generation and Thermal Rearrangement of a 2-Silaindene

Thomas J. Barton\* and Gary T. Burns

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Flash vacuum pyrolysis of a 2-allyl-2-methyl-2-silaindan affords three products: a 3-silaindene, indene, and 2-sila-1,2-dihydronaphthalene. It is proposed that these arise from rearrangement of an initially formed 2-silaindene. Chemical trapping established the intermediacy of the 2-silaindene and an isobenzosilole.

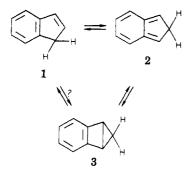
Since 1942 when Alder<sup>1</sup> reported that isoindene (2) was trapped in a [4 + 2] cycloaddition when indene (1) was heated with maleic anhydride, the thermochemistry of indenes has been extensively investigated.<sup>2</sup> It is now firmly established that indene equilibrates with isoindene via 1,5-hydrogen shifts although the presence of pseudoindene (3) in this equilibrium mixture has never been demonstrated. Pseudoindenes have been prepared and thermally isomerized to isoindenes and indenes. One other fact of interest is that in addition to hydrogen migrations, 1,5 shifts of phenyl and methyl have also been documented.

Our recent discovery<sup>3</sup> that 1-methylsilole (5) is conveniently produced from the flash vacuum pyrolysis (FVP) of 4-allyl-4-methyl-4-silacyclopentene (4) suggested that we might be able to use this route to gain entry to silaindene-silaisoindene energy surface. Thus, we synthesized the desired precursor, 2-allyl-2-methyl-2-silaindan (8) in three steps in an overall yield of 28%. Coupling of benzylmagnesium chloride with (chloromethyl)methyldi-

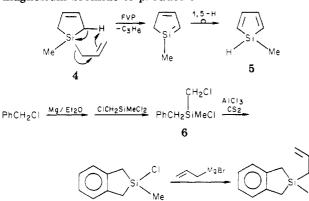
<sup>(1)</sup> Alder, K.; Pascher, F.; Vagt, H. Ber. Dtsch. Chem. Ges. 1942, 75, 1501.

<sup>(2)</sup> For a current review see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 290-294.

<sup>(3)</sup> Burns, G. T.; Barton, T. J. J. Organomet. Chem. 1981, 209, C25.



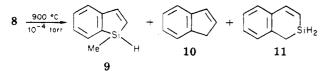
chlorosilane afforded chlorosilane 6 in 70% yield. Intramolecular Friedel-Crafts alkylation of 6 gave 2-chloro-2methyl-2-silaindan (7) that was coupled with allylmagnesium bromide to produce 8.



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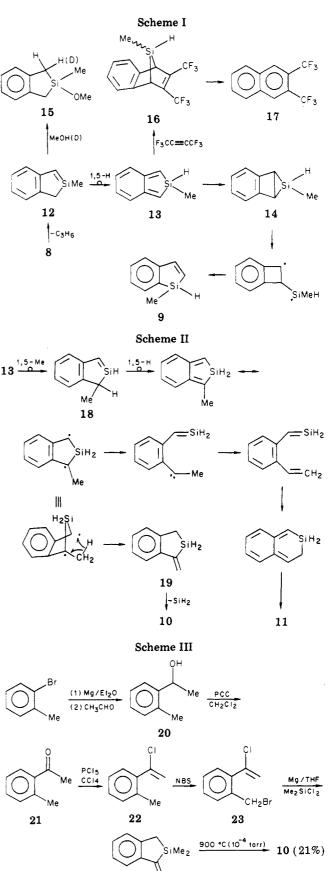
8

FVP (900 °C ( $10^{-4}$  torr), 1-ft horizontal quartz chip packed tube) of 8 produced a light yellow oil in 40% mass recovery. Analysis of the pyrolysate by GC (9 ft, 3% SE 30) revealed, in addition to unreacted 8, three major products. These were isolated by preparative GC and assigned structures 9, 10, and 11 on the basis of their <sup>1</sup>H NMR, IR, and mass spectra. Although the respective absolute yields of 9%, 11%, and 16% were low, the pyrolysate was quite clean as these three products plus residual 8 totaled 79% of the pyrolysate.



Thus, like 4, 8 also produces a silole, 9, upon pyrolysis although a novel reorganization of the ring skeleton was required. We propose that 9 is formed from 8 through a sequence of propene elimination<sup>4</sup> to form silaindene 12, 1,5-hydrogen migration to form isobenzosilole 13, ring closure to pseudosilaindene 14, Si–C bond homolysis, and 1,2-aryl migration as shown in Scheme I.

The intermediacy of 12 was confirmed by methanol trapping. Copyrolysis of 8 and MeOH (640 °C, vertical tube, N<sub>2</sub> flow, 5 mL/7 s) afforded the expected product of silene trapping, 2-methyl-2-methoxy-2-silaindan (15) in 36% yield (based on reacted 8) as the sole volatile product. That 15 did not arise from methanolysis of the allyl-silicon bond was established by copyrolysis of 8 and MeOD to obtain only 1-deuterio-2-methoxy-2-silaindan (15d). Evidence for the intermediacy of isobenzosilole 13 was less direct and was derived from copyrolysis of 8 and perfluoro-2-butyne (640 °C, vertical tube,  $F_3CC \equiv CCF_3$  as



carrier gas). Analysis of the pyrolysate by GC/MS revealed the formation of 2,3-bis(trifluoromethyl)naphthalene (17), the expected product from Diels-Alder trapping of 13 followed by the well-precedented extrusion of methylsilylene from  $16.^5$  The formation of 9, 10, and 11 was

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### Pyrolytic Generation of a 2-Silaindene

completely inhibited in both of these copyrolyses, further implying the intermediacy of 12 and 13 in their formation.

The origin of products 10 and 11 from the pyrolysis of 8 is far less certain, but one common feature is that the carbon from the silyl methyl has been incorporated into the ring. This is most easily accomplished by initial 1,5-CH<sub>3</sub> migration in 13 and thus adds another analogy with the known thermochemistry of the carbon analogues. The actual pathways from isobenzosilole (18) to 9 and 10 cannot be deduced from the present data. The schemes herewith (Scheme II) displayed are purely speculative but should serve as stimuli for further work on this intriguing system. Indeed we have recently found that the dimethyl derivative of 19, 24, undergoes FVP (900 °C ( $10^{-4}$  torr)) to afford indene (10) in 21% yield (Scheme III). It should be noted that while we synthesized o-methylacetophenone (21) from o-bromotoluene as illustrated in Scheme III, 21 is commercially available from Aldrich.

## **Experimental Section**

General Data. Proton NMR spectra were recorded on a Varian Model EM-360 spectrometer. GC mass spectral data were collected at 70 eV on a Finnegan Model 4023 mass spectrometer. Exact mass measurements were obtained on an AEI MS-902 mass spectrometer. Gas chromatographic separations were performed on a Varian-Aerograph Series 1700 gas chromatograph. Unless otherwise specified, all yields are GC yields calculated from predetermined response factors and are absolute.

Synthesis of 2-Allyl-2-methyl-2-silaindan (8). To a stirring suspension of 5.76 g (0.237 mol) of magnesium in 250 mL of ether was added 26.78 g (0.212 mol) of benzyl chloride over a 4-h interval. This Grignard solution was transferred via a double-tipped needle to a stirring solution of 34.62 g (0.211 mol) of (chloromethyl)methyldichlorosilane in 500 mL of ether. The solution was stirred for 3 h at room temperature. The solvent was then stripped via rotary evaporation and the residue taken up in hexane. Filtration of the exane followed by concentration of the filtrate afforded  $\sim$ 45 mL of a light brown oil. Distillation of the oil at 110-113 °C (0.1 torr) afforded 32.5 g (70%) of 6 [NMR (CCl<sub>4</sub>)  $\delta$  0.10 (s, 3 H), 2.13 (s, 2 H), 2.50 (s, 2 H), 7.0 (s, 5 H)], which was used without further purification. To a stirring solution of 32.5 g (0.148 mol) of 6 in 200 mL of  $CS_2$  was added 4.40 g (0.033 mol) of aluminum trichloride. After being refluxed for 12 hours, the solution was filtered through celite. The filtrate was concentrated by rotary evaporation. Distillation of the residue at 87–89 °C (0.1 torr) afforded 20.0 g (74% yield) of 2-chloro-2-methyl-2-silaindan (7) [NMR (CCl<sub>4</sub>) δ 0.58 (s, 3 H), 2.23 (s, 4 H), 7.0 (m, 4 H)], which was used without further purification. To a stirring solution of 14.07 g (0.077 mol) of 2-chloro-2-methyl-2-silaindan in 100 mL of ether at -70 °C was added 120 mL (0.096 mol) of a 0.80 M allylmagnesium bromide in ether solution. After the addition was complete, the solution was allowed to warm to room temperature. The organic solution was stirred for several hours, quenched with 10% ammonium chloride, washed with water, and dried with sodium sulfate. After removal of solvent, distillation gave 7.85 g of 8 (bp 100-102 °C (0.01 torr)): NMR (CCl<sub>4</sub>) δ 0.22 (s, 3 H), 1.67 (d, 2 H, J = 8 Hz), 2.02 (s, 4 H), 4.63–5.04 (m, CH<sub>3</sub>CH=CH<sub>2</sub>, 2 H), 5.38-6.12 (m, CH<sub>2</sub>CHCH<sub>2</sub>, 1 H), 7.0 (m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 188 (5), 147 (100), 146 (96), 145 (39), 119 (13), 105 (10), calculated for  $C_{12}H_{16}Si m/e$  188.10213, measured m/e 188.10239.

Vacuum Pyrolysis of 2-Allyl-2-methyl-2-silaindan (8). The pyrolysis of 8 was carried out by evaporating it (25 °C ( $1 \times 10^{-4}$  torr)) through a horizontal quartz tube packed with quartz chips and heated to 860 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 36% mass recovery. Three products in addition to unreacted 8 were obtained and were isolated by preparative gas chromatography on a 9 ft × 1/4 in. SE-30 on Chromosorb W column using a temperature program of 140–210 °C at 2 °C/min. The major product 11 (16%) was identified on the basis of its spectra: NMR (CCl<sub>4</sub>)  $\delta$  2.24 (t, 2 H), 4.08 (t, 2 H), 6.59 (center of AB quartet, 2 H,  $\nu_{\rm A}$  = 5.93,  $\nu_{\rm B}$  = 7.25), 7.01 (br s, 4 H); IR (neat) 3060, 3020, 2140 (Si-H), 1600, 1585, 1550, 950, 860 cm<sup>-1</sup>; mass spectrum (70 eV), m/e (% relative intensity) 146 (100), 145 (67), 143 (27), 131 (39), 119 (14), 118 (16), 117 (15), 116 (12), 115 (36), 105 (24), 53 (30), calculated for C<sub>9</sub>H<sub>10</sub>Si m/e 146.055 18, measured m/e 146.055 03. The coupling constant of 14 Hz is consistent with that expected for a *cis*-vinylsilane.<sup>6</sup> The lack of coupling between the vinyl hydrogen and the silyl hydride is also observed in 1-methyl-1-silacyclohexa-2,4-diene.

The second major product was identified as indene (11%) on the basis of its spectra: NMR (CCl<sub>4</sub>)  $\delta$  3.62 (t, 2 H, J = 2 Hz), 6.62-7.73 (m, 6 H); mass spectrum (70 eV), m/e (% relative intensity) 116 (100), 115 (89), 89 (16), 63 (16), 57 (16). All spectra fit with those of an authentic sample. The third major product was identified as 1-methylbenzosilole (9; 9.2%) on the basis of its spectra: NMR (CCl<sub>4</sub>)  $\delta$  0.38 (d, J = 4 Hz, 3 H), 4.59 (q, J =4 Hz, 1 H), 6.84 (center of AB quartet, J = 10 Hz, 2 H,  $\nu_A = 6.16$ ,  $\nu_B = 7.32$ ), 7.09-7.63 (aromatic m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 146 (100), 145 (76), 143 (11), 131 (63), 119 (12), 105 (57), 103 (10), 77 (13), 53 (39), calculated for C<sub>9</sub>H<sub>10</sub>Si m/e 146.055 18, measured 146.054 77.

Copyrolysis of 8 and Methanol. A solution consisting of 0.2649 g (1.41 mmol) of 8 and 0.8166 g (0.0255 mol) of methanol was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 640 °C. A continuous nitrogen stream of 5 mL/7 was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. The major product, 2-methyl-2-methoxy-2-silaindan (15; 36%), was isolated by preparative gas chromatography on a 6 ft  $\times 1/4$  in. SE-30 column at 190 °C and was identified on the basis of its spectra: NMR (CCl<sub>4</sub>)  $\delta$  0.30 (s, 3 H), 2.01 (center of AB quartet, 4 H, J = 18 Hz,  $\nu_A = 2.14$ ,  $\nu_B = 1.88$ ), 3.38 (s, OMe, 3 H), 7.0 (m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 178 (46), 163 (23), 146 (100), 133 (37), 131 (16), 59 (65), calculated for  $C_{10}H_{14}SiO m/e 178.08140$ , measured m/e 178.08112. Compound 15 was independently prepared by adding an equimolar mixture of pyridine and methanol to a stirring solution of 2-chloro-2-methyl-2-silaindan in pentane. After filtration to remove the precipitated pyridinium hydrochloride, the filtrate was distilled at 93-96 °C to afford a 46% yield of 15. The spectra obtained from the independently prepared 15 were identical with those reported above.

**Copyrolysis of 8 and Methanol**- $d_1$ . A solution consisting of 0.228 g (1.21 mmol) of 8 and 0.6603 g (0.020 mol) of methanol- $d_1$ was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 660 °C. A continuous nitrogen stream of 5 mL/7 s was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. The major product, 1-deuterio-2-methyl-2methoxy-2-silaindan (15d; 17%), was identified on the basis of its spectra: NMR (CCl<sub>4</sub>)  $\delta$  0.30 (s, SiMe, 3 H), 2.01 (center of AB quartet with multiplet underneath, total of 3 H,  $J_{AB} = 18$  Hz,  $v_A$ = 2.14,  $v_B = 1.88$ ), 3.38 (s, OMe, 3 H), 7.0 (m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 179 (48), 164 (26), 147 (82), 146 (46), 134 (38), 132 (14), 59 (100).

Copyrolysis of 8 and Perfluoro-2-butyne. Compound 8 (0.381 g, 2.03 mmol) was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 640 °C. Perfluoro-2-butyne (10 mL/15 s) was used as both the carrier gas and the trap. 2,3-Bis(trifluoromethyl)naphthalene (17) was isolated by preparative gas chromatography and identified on the basis of its spectra: NMR (CDCl<sub>3</sub>)  $\delta$  7.33-8.43 (m); mass spectrum (70 eV), m/e (% relative intensity) 264 (100), 245 (32), 214 (41) 195 (47), 175 (26), 159 (29), 145 (13), 126 (15), 125 (19), 99 (14), 98 (36), 75 (23), 74 (25), 69 (31), 63 (18), 62 (13).

Synthesis of 20. A 1-L three-necked round-bottom flask was fitted with a reflux condensor with drying tube, a pressureequilized addition funnel with a nitrogen inlet, and a stirring bar. The apparatus was flame dried under a stream of nitrogen and then charged with 5.61 g (0.231 mol) of magnesium turnings and 100 mL of ether. To this stirring solution was added 34.2 g (0.200 mol) of o-bromotoluene over a 2.5-h interval. After the Grignard formation had begun, the solution was further diluted with 400 mL of ether. To the stirring Grignard solution was added 11.82 g (0.268 mol) of acetaldehyde at a rate to maintain a steady reflux. Stirring was continued for 1.5 h after the addition was complete. The organic solution was then quenched with 125 mL of 0.1 N HCl, washed with water, and dried over sodium sulfate. After filtration, distillation of the filtrate at 99-101 °C (1.0 torr) afforded 17.30 g (64%) of 20 (lit.<sup>7</sup> bp 120-130 °C (29.0 torr)).

PCC Oxidation of 20 to 21. To a stirring suspension of 105 g (0.486 mol) of pyridinium chlorochromate (PCC) in 500 mL of methylene chloride was added 33.0 g (0.243 mol) of 20 over a 15-min period. The solution immediately turned black. After being stirred for 2.5 h at room temperature, the solution was filtered through celite and the filtrate concentrated by rotary evaporation. The residue was taken up in hexane and filtered through celite and the hexane removed to afford 27.84 g (85%) of 21 as a light orange liquid: NMR (CCl<sub>4</sub>)  $\delta$  2.33 (s, 3 H), 2.37 (s, 3 H), 6.95–7.60 (m, 4 H). This ketone is available from Aldrich Chemical Co., and their NMR spectrum of 20 in the "Aldrich Library of NMR Spectra" shows both methyls as a single peak at ca.  $\delta$  2.5 in DCCl<sub>3</sub> solution. The IR spectrum of 20 matched that given in the "Aldrich Library of Infrared Spectra".

Synthesis of 22.8 To a stirring solution of 40.0 g (0.192 mol) of phosphorus pentachloride in 200 mL of CCl<sub>4</sub> at 65 °C was added 24.55 g (0.183 mol) of 21. After being stirred for approximately 3 h at 65 °C, the reaction was stopped and the solvent removed by rotary evaporation. The residue was eluted through silica gel with hexane to afford 24.0 g (87%) of compound 22: NMR (CCl<sub>4</sub>) δ 2.39 (s, 3 H), 5.27 (br s, 1 H), 5.57 (br s, 1 H), 7.12 (br s, 4 H).

Synthesis of 23. A solution of 4.599 g (0.030 mol) of 22, 5.46 g (0.0307 mol) of N-bromosuccinimide, and 80 mL of CCl<sub>4</sub> was refluxed for several hours and then filtered through celite. The filtrate was concentrated by rotary evaporation. Elution of the residue through silica gel with hexane afforded 5.244 g (76%) of **23:** NMR ( $\dot{CCl}_4$ )  $\delta$  4.59 (s, 2 H), 5.60 (d, J = 1 Hz, 1 H), 5.73 (d, J = 1 Hz, 1 H), 7.32 (m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 232 (11), 230 (14), 152 (90), 144 (80), 116 (100), 114 (95), 89 (65), 55 (95), 53 (75), calculated for  $C_9H_8BrCl m/e$ 229.94979, measured m/e 229.94897.

Ring Closure of 23 to 24. To a stirring solution of 2.66 g (0.0266 mol) of dimethyldichlorosilane, 1.217 g (0.050 mol) of magnesium powder, and 80 mL of dry THF was added 4.522 g (0.0195 mol) of 23 over a 45-min period at a rate sufficient to maintain a slow reflux. After being stirred for 11 h at room temperature, the organic solution was poured into hexane and filtered. The filtrate was carefully concentrated by rotary evaporation. Distillation of the residue at 79-81 °C (0.1 torr) afforded 0.559 g (16%) of 24: NMR (CCl<sub>4</sub>) & 0.26 (s, 6 H), 2.00 (s, 2 H), 5.38 (d, 1 H, J = 2 Hz), 6.12 (d, 1 H, J = 2 Hz), 6.90-7.55(m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 174 (78), 159 (100), 143 (11), 133 (23), 131 (48), 115 (22), 105 (18), 77 (10), 59 (44), 53 (17), calculated for  $C_{11}H_{14}Si \ m/e \ 174.08648$ , measured m/e 174.08541.

Vacuum Pyrolysis of 24. The pyrolysis of 24 was carried out by evaporating  $(25 \text{ °C} (1 \times 10^{-4} \text{ torr})) 0.7254 \text{ g} (4.17 \text{ mmol})$  through a quartz tube packed with quartz chips and heated to 920 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 79% (0.571 g) mass recovery. Indene (21%) was identified by comparison of its GC retention time and GC mass spectrum with those of an authentic sample. The other major volatile material was identified as unreacted 24 on the basis of its GC mass spectrum and GC retention time.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation for this work.

Registry No. 1, 95-13-6; 6, 66817-66-1; 7, 82880-79-3; 8, 82880-80-6; 9, 82880-81-7; 11, 82880-82-8; 15, 82880-83-9; 15d, 82880-84-0; 17, 50318-09-7; 20, 7287-82-3; 21, 577-16-2; 22, 38379-19-0; 23, 82880-85-1; 24, 82880-86-2; perfluoro-2-butyne, 692-50-2; phosphorus pentachloride, 10026-13-8; benzyl chloride, 100-44-7; (chloromethyl)methyldichlorosilane, 1558-33-4; methanol, 67-56-1; obromotoluene, 95-46-5; acetaldehyde, 75-07-0; dimethyldichlorosilane, 75-78-5; magnesium, 7439-95-4.

# Synthesis and Properties of the Geometrical Isomers of *tert*-Butylmethylcyclosilanes, (t-BuMeSi)<sub>4</sub> and (t-BuMeSi)<sub>5</sub>

Bradley J. Helmer and Robert West\*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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Coupling of t-BuMeSiCl<sub>2</sub> with Li provides the four-silicon ring compound 1,2,3,4-tetra-tert-butyltetramethylcyclotetrasilane  $(t-BuMeSi)_4$  (1) in an 85% yield, as a mixture of the four possible isomers. The isomers have been separated, identified, and characterized by UV, <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy. The four isomers of the five-membered ring  $(t-BuMeSi)_5$  (2) have also been identified. The isomeric distribution of 1 is substantially altered by photolysis or reaction with Na/K. The radical anions of both 1 and 2 have been studied by ESR, with 1- showing remarkable stability and a well-resolved spectrum of more than 30 lines.

### Introduction

Earlier papers from this laboratory<sup>1-4</sup> described the synthesis of 1,2,3,4-tetra-tert-butyltetramethylcyclotetra-

silane,  $(t-BuMeSi)_4$  (1), by reductive coupling of t-Bu-MeSiCl<sub>2</sub> with Na/K alloy in refluxing tetrahydrofuran (THF). Two of the four isomers, 1a and 1b, were identified, and evidence was also found for a third isomer.<sup>1</sup> Isomer 1a was shown to be the all-trans structure by means of an X-ray diffraction study,<sup>3</sup> and 1b was uniquely identified from its 1:2:1 <sup>1</sup>H NMR spectrum. The electronic and photoelectron spectra of 1a were investigated.<sup>4</sup> In spite of the obvious strain in the silicon ring, 1a and 1b were found to be remarkably inert chemically, evidently

<sup>(7)</sup> Hirschberg, V. J. Am. Chem. Soc. 1949, 71, 3241.

<sup>(8)</sup> This is a slight modification of the synthetic procedure for 22 reported by Yates.<sup>9</sup>

<sup>(9)</sup> Yates, K.; Mandrapilias, G. J. Org. Chem. 1980, 45, 3892.

Biernbaum, M.; West, R. J. Organomet. Chem. 1977, 131, 179.
Biernbaum, M.; West, R. J. Organomet. Chem. 1977, 131, 189.
Hurt, C. J.; Calabrese, J. C.; West, R. J. Organomet. Chem. 1975, 91, 273.

<sup>(4)</sup> Block, T. R.; Biernbaum, M.; West, R. J. Organomet. Chem. 1977, 131. 199.