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Silicon–Carbon Unsaturated Compounds. 35. Thermolysis of 3,4-Benzo-1,1,2,2-tetraethyldisilacyclobutene

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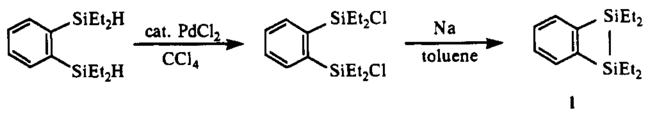
Thermolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (1) at 250 °C gave 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (4). Similar thermolysis of 1 with *tert*-butyl alcohol produced 1-(*tert*-butoxydiethylsilyl)-2-(diethylsilyl)benzene. The reaction of compound 1 with phenylacetylene, 1-hexyne, and dimethyl acetylenedicarboxylate afforded the respective [4 + 2] cycloadducts arising from *o*-quinodisilane and the acetylenes. Similarly, heating 1 with benzaldehyde and formaldehyde yielded the corresponding [4 + 2] cycloadducts, while with methyl vinyl ketone 1 gave an eight-membered cyclic compound, 7,8-benzo-1,1,6,6-tetraethyl-3-methyl-2-oxa-1,6-disilacycloocta-3,7-diene.

Introduction

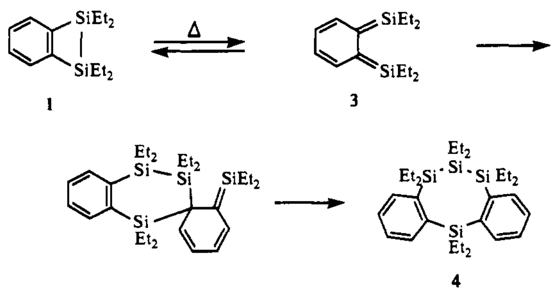
Since the first evidence for the formation of 1,1-dimethylsilene has been reported by Gusel'nikov and Flowers in 1967,[1] many papers concerning the preparation and reactions of the silenes have been published to date.[2-4] The formation and reactions of unsaturated silicon compounds that have a conjugated double bond, 1-silabuta-1,3-dienes[5,6] and *o*-silaquinone methides,[7,8] have also been reported. However, little interest has been shown in the chemistry of 1,4-disilabuta-1,3-dienes. In 1976, Barton and Kilgour reported that the thermolysis of 1,1,2,2,3,4-hexamethyl-1,2-disilacyclobutene in the presence of 2-butyne and 3-hexyne at 225 °C gives 1,4-disilacyclohexa-2,5-dienes in low yields, together with a large amount of hexamethyl-1,3-disila-2-oxacyclopent-4-ene.[9] They proposed the intermediacy of hexamethyl-1,4-disilabuta-1,3-diene to explain the formation of the 1,4-disilacyclohexa-2,5-dienes. Sakurai and his co-workers have reported the thermolysis of 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disilacyclobutene with diphenylacetylene at 350 °C, leading to 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene. However, they obtained the product only in 1.2% yield.[10] We have also investigated the thermolysis of 1,1,2,2-tetramethyl-4-phenyl-3-(trimethylsilyl)-1,2-disilacyclobutene in the presence of phenyl(trimethylsilyl)acetylene. In this reaction, no evidence for the formation of the 1,4-disilabuta-1,3-diene could be obtained.[11]

We attempted to investigate the chemical behavior of *o*-quinodisilane and used a 3,4-benzodisilacyclobutene as a precursor of these compounds. To our knowledge, the first example of the preparation and reactions of the benzodisilacyclobutene has been reported by Shiina.[12] He found that the reaction of 1,2-bis(chlorodimethylsilyl)benzene with sodium affords 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene and treatment of this compound with a catalytic amount of anhydrous aluminum chloride in toluene at 0 °C or heating the compound in toluene at 60 °C gave poly[*o*-(tetramethyldisilanylene)phenylene] with high molecular weight.

Scheme I



Scheme II



In this paper, we report the thermolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene in the presence or absence of a trapping agent in a degassed sealed tube, in which all results can best be explained in terms of the formation of 1,2-bis(diethylsilylene)cyclohexa-3,5-diene (*o*-quinodisilane).

Results and Discussion

The starting compound, 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (1), could be readily prepared by the similar method reported by Shiina.[12] Thus, the reaction of *o*-dibromobenzene with magnesium in the presence of 2 equiv of chlorodiethylsilane in THF afforded 1,2-bis(diethylsilyl)benzene in 55% yield. Hydrogen–chlorine exchange of the bis(diethylsilyl)benzene in the presence of a catalytic amount of palladium dichloride in carbon tetrachloride gave 1,2-bis(chlorodiethylsilyl)benzene in 80% yield. Finally, sodium condensation of the resulting bis(chlorosilyl)benzene yielded compound 1 in 75% yield (Scheme I). In sharp contrast to 3,4-benzotetramethyldisilacyclobutene reported by Shiina, compound 1 is rather thermally stable and can be isolated by distillation under reduced pressure. Compound 1, however, is gradually oxidized in air at room temperature to give 4,5-benzo-2-oxa-1,3-disilacyclopentene (2). It is well-known that the 1,2-disilacyclobutenes are readily oxidized in air, giving

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[1] Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* **1967**, 864.
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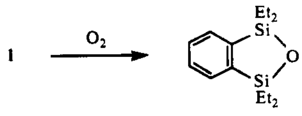


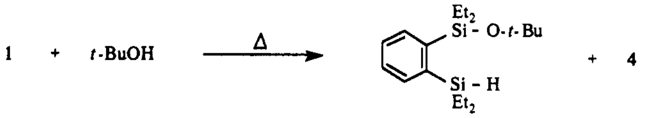
2

1,3-disila-2-oxacyclopentenes.[9,10,13]

First, we carried out the thermolysis of 1 in the absence of a trapping agent. Thus, heating 1 at 250 °C in a sealed degassed tube for 24 h gave an unexpected product, 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (4), in 72% yield, in addition to 5% of the unchanged starting compound 1 (Scheme II). The structure of 4 was confirmed by spectrometric analysis, as well as by elemental analysis. The ^{29}Si NMR spectrum of 4 reveals three resonances at −38.94, −11.89, and −5.66 ppm, due to the three kinds of silicon atoms. Its ^{13}C NMR spectrum also indicates the presence of three different diethylsilyl groups at 0.70, 5.50, 6.81, 7.60, 8.51, and 10.89 ppm, as well as six signals attributed to phenylene ring carbons. These results are wholly consistent with the proposed structure. The formation of the product 4 can best be understood in terms of bimolecular [4 + 2] cycloaddition of the *o*-quinodisilane (3), followed by ring enlargement to the eight-membered cyclic system. The dimerization leading to a spiro compound has been observed in the *o*-quinodimethane chemistry.[14]

Interestingly, similar thermolysis of 1 with a 10-fold excess of isopropylbenzene under the same conditions gave the dimer 4 in only 4% yield. In this reaction, 88% of the starting benzodisilacyclobutene 1 was recovered unchanged. Presumably, the *o*-quinodisilane 3 is transformed into the starting compound 1 by intramolecular recombination.

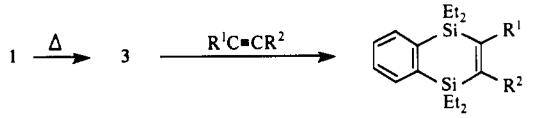
In order to obtain more information about the chemical behavior of the reactive intermediate involved in this thermolysis, we carried out the thermolysis of 1 in the presence of *tert*-butyl alcohol as a trapping agent. Heating 1 with 1.6 equiv of *tert*-butyl alcohol at 250 °C for 24 h afforded 1-(*tert*-butoxydiethylsilyl)-2-(diethylsilyl)benzene (5) in 13% yield, in addition to 60% of the dimer 4. As expected, the higher concentration of *tert*-butyl alcohol gives the adduct 5 in higher yield. Thus, the thermolysis of 1 with 4 equiv of *tert*-butyl alcohol gave compound 5 in 40% yield, along with 53% of the dimerization product 4. It has been found that the thermolysis of benzosilacyclobutenes with alcohols produces two products, alkoxy-*o*-tolylsilanes and alkoxybenzylsilanes.[8] The present reaction, however, gave only the product arising from 1,4-addition of *tert*-butyl alcohol to the *o*-quinodisilane.



5

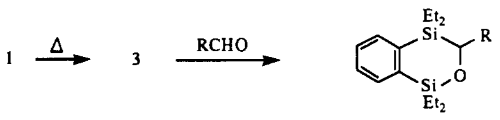
The IR spectrum of 5 shows a strong absorption at 2152 cm^{-1} due to Si–H stretching frequencies. The ^{1}H NMR spectrum of 5 also reveals quintet signals at 4.61 ppm (J = 3.3 Hz) attributed to an Si–H proton, as well as a singlet resonance at 1.31 ppm due to *tert*-butyl protons.

Scheme III



6. R^1=Ph, R^2=H
7. R^1=Bu, R^2=H
8. R^1=R^2=C(O)OMe

Scheme IV



9. R=Ph
10. R=H

The benzodisilacyclobutene 1 reacts readily with acetylenes at 250 °C. The thermolysis of 1 with 2.5 equiv of phenylacetylene under the same conditions afforded 2,3-benzo-1,1,4,4-tetraethyl-5-phenyl-1,4-disilacyclohexa-2,5-diene (6) arising from [4 + 2] cycloaddition of the *o*-quinodisilane 3 and phenylacetylene in 89% yield, as the sole product (Scheme III). Similarly, the thermolysis of 1 with 2 equiv of 1-hexyne afforded 2,3-benzo-5-butyl-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (7) in 67% yield, in addition to 5% of the dimer 4. Dimethyl acetylenedicarboxylate also reacted under the same conditions to give 5,6-benzo-2,3-dicarbomethoxy-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (8) in 83% yield. The ^{13}C NMR spectrum of 8 exhibits two resonances at 5.95 and 7.42 ppm due to ethyl carbons and three resonances at 128.5, 133.3, and 140.8 ppm attributed to phenyl carbons, as well as signals at 153.9 and 169.9 ppm due to olefinic and carbonyl carbons, respectively. This result is consistent with the proposed structure. In marked contrast to hexamethyl-1,2-disilacyclobutene reported by Barton and Kilgour,[9] compound 1 did not react with disubstituted acetylene such as diphenylacetylene and 3-octyne under the same conditions. In these thermolyses, the dimerization product 4 was always obtained in high yields. The structures of the acetylene adducts 6–8 were confirmed by IR, mass, and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis.

Unfortunately, the present *o*-quinodisilane did not react with olefins such as 1-hexene and 2,3-dimethyl-1,3-butadiene. In these reactions, again the dimer 4 was produced in high yields.

The *o*-quinodisilane 3, however, reacted with aldehydes to give [4 + 2] cycloadducts. Thus, heating 1 with 7.5 equiv of benzaldehyde at 250 °C for 24 h yielded 5,6-benzo-1,1,4,4-tetraethyl-3-phenyl-1,4-disila-2-oxacyclohexane (9) and compound 4 in 52 and 12% yields, respectively (Scheme IV). Similar reaction of 1 with 6 equiv of paraformaldehyde under the same conditions produced a [4 + 2] cycloadduct, 5,6-benzo-1,1,4,4-tetraethyl-1,4-disila-2-oxacyclohexene (10) in 88% yield, as the sole product. The thermolysis of 1 with acetone under the same conditions afforded no addition product analogous to 9 and 10, but the dimer 4 was obtained in 30% yield, in addition to a 45% yield of the starting compound 1.

Weber and his co-workers have reported that gas-phase pyrolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene with acetone or formaldehyde produces a mixture of products arising from [2 + 2] and [4 + 2] cycloaddition reactions of a 1-silabutadiene intermediate with carbonyl compounds.[6] In the present reactions, however, no prod-

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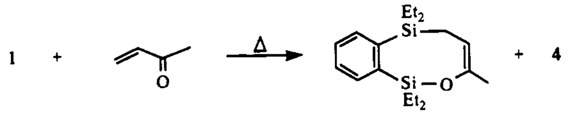
[14] (a) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 1949. (b) Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820.

ucts derived from [2 + 2] cycloaddition of the *o*-quinodisilane with aldehydes were detected by either spectrometric analysis or GLC analysis.

We have also carried out the reaction of the *o*-quinodisilane with an enone. To our surprise, when compound 1 was heated with 2.5 equiv of methyl vinyl ketone under the same conditions, 7,8-benzo-1,1,6,6-tetraethyl-3-methyl-2-oxa-1,6-disilacycloocta-3,7-diene (11) was obtained in 30% yield, together with 57% of the dimer 4.



11

Since the present *o*-quinodisilane does not react with acetone and olefins, the mechanism involving [4 + 4] cycloaddition seems to be more attractive for the formation of compound 11 than that involving [2 + 2] cycloaddition, followed by ring enlargement to the eight-membered cyclic system.

The structures of 9–11 were verified by spectrometric analysis as well as by elemental analysis (see the Experimental Section).

In conclusion, the thermolysis of 1 affords *o*-quinodisilane. The *o*-quinodisilane 3 thus formed undergoes bimolecular [4 + 2] cycloaddition, followed by ring enlargement to the eight-membered cyclic system in the absence of a trapping agent. Compound 3 reacts with acetylenes and aldehydes to give [4 + 2] cycloadducts, while with methyl vinyl ketone gives an eight-membered cyclic adduct.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry argon. Thermolysis were carred out in a 8 cm × 6 mm degassed sealed tube at 250 °C. Yields were determined by GLC using an internal standard. Infrared spectra were obtained with the use of Perkin-Elmer 1600 FT infrared spectrometer. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were determined with a JEOL Model EX-270 spectrometer using deuteriochloroform as a solvent. Mass spectra were measured on Shimadzu Model QP-1000 instrument. Gas chromatographic separations were carried out using a column (3 m × 10 mm) packed with 30% SE-30 silicone on Chromosorb P.

Preparation of 1,2-Bis(diethylsilyl)benzene. In a 500-mL four-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 11.4 g (0.47 mol) of magnesium and 57.3 g (0.47 mol) of diethylchlorosilane in 280 mL of THF. To this was added a solution of 53.6 g (0.23 mol) of *o*-dibromobenzene dissolved in 20 mL of THF over a period of 2 h at room temperature. The mixture was heated to reflux for 3 h and then cooled to room temperature. To this was added 200 mL of hexane, and the resulting salts were filtered off. The solvents were evaporated, and the residue was fractionally distilled under reduced pressure to give 31.2 g (55% yield) of colorless liquid: bp 75–78 °C (2 mmHg); MS *m/e* 250 (M$^+$); IR 2137, 1458, 1414, 1378, 1119 cm^{-1}; ^{1}H NMR 0.79–1.12 (m, 20 H, EtSi), 4.29–4.55 (m, 2 H, HSi), 7.05–7.55 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 4.50, 8.35 (EtSi), 128.0, 135.1, 142.9 ppm (phenylene ring carbons). Anal. Calcd for $C_{14}H_{26}Si_2$: C, 67.12; H, 10.46. Found: C, 67.12; H, 10.40.

Preparation of 1,2-Bis(chlorodiethylsilyl)benzene. In a 200-mL two-necked flask fitted with a stirrer and reflux condenser was placed 31.2 g (0.13 mol) of 1,2-bis(diethylsilyl)benzene in 80 mL of carbon tetrachloride. To this was added 0.20 g (1.13 mmol) of palladium dichloride. At this time, the exothermic reaction took place. After the temperature of the mixture dropped, the mixture was heated to reflux for 45 h. The solvents were evaporated, and the residue of the flask was distilled under reduced pressure to give 32.0 g (80% yield) of pale yellow liquid: bp 115–118 °C (2 mmHg); MS *m/e* 318 (M$^+$); IR 1462, 1380, 1118, 1041, 1006 cm^{-1}; ^{1}H NMR 0.85–1.25 (m, 20 H, EtSi), 7.02–7.82 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 6.99, 10.30 (EtSi), 128.8, 136.2, 142.0 ppm (phenylene ring carbons). Anal. Calcd for $C_{14}H_{26}Cl_2Si_2$: C, 52.64; H, 7.57. Found: C, 52.60; H, 7.56.

Preparation of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (1). In a 200-mL two-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 5.6 g (0.24 mol) of sodium and 80 mL of toluene. The contents of the flask were heated to reflux, and then a solution of 32.0 g (0.10 mol) of 1,2-bis(chlorodiethylsilyl)benzene in 10 mL of toluene was added over a period of 2 h. After the mixture was heated to reflux for 16 h, the solvents were distilled off. The residue of the flask was distilled under reduced pressure to give 18.5 g (75% yield) of colorless liquid: bp 80–82 °C (2 mmHg); MS *m/e* 248 (M$^+$); IR 1459, 1413, 1376, 1257, 1233, 1113 cm^{-1}; ^{1}H NMR 0.79–1.29 (m, 20 H, EtSi), 7.03–7.63 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 5.71, 8.80 (EtSi), 128.8, 132.2, 155.6 ppm (phenylene ring carbons); ^{29}Si NMR (C_6D_6) 8.05 ppm. Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73. Found: C, 67.42; H, 9.67.

Oxidation of 1. Compound 1 (0.1077 g, 0.434 mmol) was allowed to stand in air for 120 h. GLC analysis showed that 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopentene (2) was produced quantitatively. Compound 2: MS *m/e* 264 (M$^+$); IR 1460, 1427, 1410, 1377, 1259, 1235, 1051 cm^{-1}; ^{1}H NMR 0.78–1.01 (m, 20 H, EtSi), 7.15–7.46 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 6.58, 7.28 (EtSi), 128.7, 136.1, 146.8 ppm (phenylene ring carbons); ^{29}Si NMR 16.97 ppm. Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.15. Found: C, 63.38; H, 9.11.

Thermolysis of 1. Compound 1 (1.682 g, 6.78 mmol) was heated at 250 °C in a degassed sealed tube for 24 h. GLC analysis of the reaction mixture indicated the presence of 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (4) (72% yield) and the starting compound 1 (5% yield). Pure 4 was isolated by preparative GLC: MS *m/e* 410 (M$^+$ – SiEt$_2$); IR 1459, 1414, 1375, 1231, 1108 cm^{-1}; ^{1}H NMR 0.81–1.16 (m, 40 H, EtSi), 7.30–7.69 ppm (m, 8 H, phenylene ring protons); ^{13}C NMR 0.70, 5.50, 6.81, 7.60, 8.50, 10.89 (EtSi), 127.6, 128.0, 133.6, 134.0, 143.0, 149.4 ppm (phenylene ring carbons); ^{29}Si NMR –38.94, –11.89, –5.66 ppm. Anal. Calcd for $C_{28}H_{48}Si_4$: C, 67.66; H, 9.73. Found: C, 67.41; H, 9.73.

Thermolysis of 1 with Isopropylbenzene. A mixture of 0.1680 g (0.471 mmol) of 1 and 0.5793 g (4.83 mmol) of isopropylbenzene was heated at 250 °C in a degassed sealed tube for 24 h. GLC analysis showed the presence of dimer 4 (4% yield), in addition to 88% of the starting compound 1. All spectral data obtained for compound 4 were identical with those of authentic sample.

Thermolysis of 1 with *tert*-Butyl Alcohol. A mixture of 0.1548 g (0.624 mmol) of 1 and 0.2021 g (2.73 mmol) of *tert*-butyl alcohol was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 1-(*tert*-butoxydiethylsilyl)-2-(diethylsilyl)benzene (5) (40% yield) and 4 (53% yield). Pure 5 was isolated by preparative GLC: MS *m/e* 293 (M$^+$ – Et); IR 2152, 1458, 1059, 1018 cm^{-1}; ^{1}H NMR 0.79–0.99 (m, 20 H, EtSi), 1.31 (s, 9 H, *t*-Bu), 4.61 (quint, 1 H, HSi, J = 3.3 Hz), 7.31–7.74 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 4.60, 7.19, 8.34, 8.89 (EtSi), 32.1 (Me$_3$C), 72.9 (CMe$_3$), 127.6, 127.7, 134.8, 135.3, 142.3, 144.9 ppm (phenylene ring carbons); ^{29}Si NMR –9.55, 0.66 ppm. Anal. Calcd for $C_{18}H_{34}OSi_2$: C, 67.01; H, 10.62. Found: C, 67.05; H, 10.36.

Thermolysis of 1 with Phenylacetylene. A mixture of 0.1010 g (0.407 mmol) of 1 and 0.1387 g (1.36 mmol) of phenylacetylene was heated at 250 °C in a sealed tube for 24 h. GLC analysis of the reaction mixture showed the presence of 2,3-benzo-1,1,4,4-tetraethyl-5-phenyl-1,4-disilacyclohexa-2,4-diene (6) (89% yield). Pure 6 was isolated by preparative GLC: MS *m/e* 350 (M$^+$); IR 1488, 1440, 1204, 1162 cm^{-1}; ^{1}H NMR 0.74–0.99 (m, 20 H, EtSi), 6.89 (br s, 1 H, HC=C), 7.24–7.59 ppm (m, 9 H, phenyl and phenylene ring protons); ^{13}C NMR 6.22, 6.33, 7.51, 7.73 (EtSi), 126.3, 126.4, 127.8, 128.1, 133.2, 133.4, 143.0 (2 C), 147.9 (phenyl and phenylene ring carbons), 145.6 (HC=C), 161.1 ppm (C=CH); ^{29}Si NMR –14.58, –12.60 ppm. Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.36; H, 8.62.

Thermolysis of 1 with 1-Hexyne. A mixture of 0.4051 g (1.63 mmol) of 1 and 0.2666 g (3.25 mmol) of 1-hexyne was heated at 250 °C in a sealed tube for 24 h. GLC analysis showed that

2,3-benzo-5-butyl-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,4-diene (7) and 4 were produced in 67% and 5% yields, respectively. Pure 7 was isolated by preparative GLC: MS *m/e* 301 (M^+ - Et); IR 1560, 1414, 1377, 1231, 1127, 1001 cm^{-1}; ^1H NMR 0.67-0.89 (m, 20 H, EtSi), 0.91-0.96 (t, 3 H, CH_3, J = 7.1 Hz), 1.29-1.55 (m, 4 H, CH_2CH_2), 2.15-2.26 (m, 2 H, CH_2), 6.61 (br s, 1 H, HC=C), 7.29-7.52 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 5.95, 6.35, 7.64, 7.69 (EtSi), 14.1, 22.7, 30.6, 38.9 (C_4H_9), 127.6, 127.8, 133.1, 133.3, 143.2, 143.7 (phenylene ring carbons), 139.5 (HC=C), 162.2 ppm (C=CH): ^{29}Si NMR -15.08, -13.37 ppm. Anal. Calcd for $C_{20}H_{34}Si_2$: C, 72.65; H, 10.36. Found: C, 72.44; H, 10.23.

Thermolysis of 1 with Dimethyl Acetylenedicarboxylate. A mixture of 0.1555 g (0.627 mmol) of 1 and 0.2011 g (1.42 mmol) of dimethyl acetylenedicarboxylate was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 5,6-benzo-2,3-dicarbomethoxy-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,3-dicarbomethoxy-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (8) (83% yield) and 7% of the starting compound 1. Pure 8 was isolated by preparative GLC: MS *m/e* 390 (M^+); IR 1714, 1462, 1454, 1433, 1217, 1121 cm^{-1}; ^1H NMR 0.81-0.95 (m, 20 H, EtSi), 3.78 (s, 6 H, MeO), 7.39-7.55 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 5.95, 7.42 (EtSi), 51.9 (MeO), 128.5, 133.3, 140.8 (phenylene ring carbons), 153.9 (C=C), 169.9 ppm (C=O); ^{29}Si NMR -9.55 ppm. Anal. Calcd for $C_{20}H_{30}O_4Si_2$: C, 61.49; H, 7.74. Found: C, 61.46; H, 7.80.

Thermolysis of 1 with Diphenylacetylene. A mixture of 0.1707 g (0.688 mmol) of 1 and 0.2912 g (1.63 mmol) of diphenylacetylene was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 4 (55% yield) and unchanged 1 (20% yield).

Thermolysis of 1 with 3-Octyne. A mixture of 0.1633 g (0.659 mmol) of 1 and 0.2573 g (2.33 mmol) of 3-octyne was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 4 (32% yield) and unchanged 1 (64% yield).

Thermolysis of 1 with 1-Hexene. A mixture of 0.1707 g (0.688 mmol) of 1 and 0.0992 g (1.18 mmol) of 1-hexene was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 4 (68% yield).

Thermolysis of 1 with 2,3-Dimethyl-1,3-butadiene. A mixture of 0.2236 g (0.902 mmol) of 1 and 0.2921 g (3.56 mmol) of 2,3-dimethyl-1,3-butadiene was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 4 (38% yield) and unchanged 1 (43% yield).

Thermolysis of 1 with Benzaldehyde. A mixture of 0.2841 g (1.15 mmol) of 1 and 0.9136 g (8.62 mmol) of benzaldehyde was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 5,6-benzo-3-phenyl-1,1,4,4-tetraethyl-2-oxa-1,4-disilacyclohexa-2,5-diene (9) (52% yield) and 4 (12% yield). Pure 9 was isolated by preparative GLC: MS *m/e* 354 (M^+); IR 1456, 1120, 1026, 830 cm^{-1}; ^1H NMR 0.98-1.09 (m, 20 H, EtSi), 5.18 (s, 1 H, HC), 7.30-7.55 ppm (m, 9 H, phenyl and phenylene ring protons); ^{13}C NMR 1.82, 2.59, 6.45, 6.72, 6.81, 7.11, 7.28, 7.51 (EtSi), 67.9 (HC), 124.4, 125.4, 128.1 (2 C), 128.2, 132.8, 134.0, 141.8, 143.4, 143.7 ppm (phenyl and phenylene ring carbons); ^{29}Si NMR -8.51, 7.10 ppm. Anal. Calcd For $C_{21}H_{30}OSi_2$: C, 71.12; H, 8.53. Found: C, 70.95; H, 8.45.

Thermolysis of 1 with Paraformaldehyde. A mixture of 0.1813 g (0.731 mmol) of 1 and 0.1325 g (4.41 mmol for HCHO) of paraformaldehyde was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-1,4-disilacyclohexa-2,5-diene (10) (88% yield). Pure 10 was isolated by preparative GLC: MS *m/e* 278 (M^+); IR 1461, 1226, 1108, 1002, 973 cm^{-1}; ^1H NMR 0.74-0.99 (m, 20 H, EtSi), 3.91 (s, 2 H, H_2C), 7.33-7.51 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 3.88, 6.27, 6.90, 7.48 (EtSi), 53.9 (H_2C), 128.2 (2 C), 132.7, 133.7, 142.5, 143.4 ppm (phenylene ring carbons); ^{29}Si NMR -11.10, 6.98 ppm. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.62; H, 9.41.

Thermolysis of 1 with Acetone. A mixture of 0.1124 g (0.453 mmol) of 1 and 0.0513 g (0.884 mmol) of acetone was heated at 250 °C in a sealed tube for 24 h. The reaction mixture was analyzed by GLC as being 4 (30% yield) and unchanged 1 (45% yield).

Thermolysis of 1 with Methyl Vinyl Ketone. A mixture of 0.2406 g (0.970 mmol) of 1 and 0.1342 g (1.92 mmol) of methyl vinyl ketone was heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by GLC as being 7,8-benzo-1,1,6,6-tetraethyl-3-methyl-2-oxa-1,6-disilacycloocta-3,7-diene (11) (30% yield) and 4 (57% yield). Pure 11 was isolated by preparative GLC: MS *m/e* 318 (M^+); IR 1418, 1318, 1168, 1013 cm^{-1}; ^1H NMR 0.77-1.00 (m, 20 H, EtSi), 1.54 (br d, 2 H, H_2C, J = 7.9 Hz), 1.75 (br s, 3 H, Me), 4.71 (br t, 1 H, HC=C, J = 7.9 Hz), 7.29-7.62 ppm (m, 4 H, phenylene ring protons); ^{13}C NMR 6.20, 6.86, 7.10, 7.73 (EtSi), 10.5 (H_2C), 22.0 (Me), 103.5 (HC=C), 127.5, 128.2, 134.5, 135.5, 142.4, 144.4 (phenylene ring carbons), 146.7 ppm (C=CH). Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.69; H, 9.49.

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A Triptycene Complex of Tin(II): $[(C_{20}H_{14})SnCl(AlCl_4)]_2$

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Triptycene ($C_{20}H_{14}$) reacts with equimolar quantities of anhydrous $SnCl_2$ and $AlCl_3$ in benzene to give a crystalline complex $[(C_{20}H_{14})SnCl(AlCl_4)]_2 \cdot 2C_6H_6$. [Triclinic, space group $P\bar{1}$, a = 10.404 (3) Å, b = 13.343 (3) Å, c = 11.194 (2) Å, α = 98.63 (2)°, β = 109.23 (2)°, γ = 105.77 (2)°, V = 1375.3 Å^3, Z = 1, R_W = 0.032 for 298 refined parameters and 3597 unique reflections with $F_o \geq 4.0\sigma(F_o)$.] According to the X-ray crystal structure analysis, the compound features discrete centrosymmetrical dinuclear complex units, with each tin atom η^6-coordinated to two neighboring benzene rings of a triptycene ligand but at different metal-ring distances (2.90 and 3.38 Å). The angle between the two coordinated arene rings is contracted to 108.2°, as compared to 120° in the parent hydrocarbon. The ψ-octahedral coordination sphere of the Sn(II) centers is completed by two tin-bridging chlorine atoms and a chelating tetrachloroaluminate ligand. The benzene of crystallization is not engaged in metal complexation. A lead(II) complex $[(C_{20}H_{14})Pb \cdot (AlCl_4)_2 \cdot 0.5C_6H_6]$ has also been prepared and characterized by analytical data.

Introduction

Triptycene is a very special hydrocarbon with regard to its ligand properties for metals: In a relatively rigid molecular geometry of point group D_{3h} symmetry, it features three eqivalent benzene rings mutually inclined by 120° angles.[1] At first glance, it would appear that this molecule

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