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Oxidation of dodecamethylcyclohexasilane by m-chloroperbenzoic acid

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permit firm conclusions on the nature of the surface cyclopentadienyl species. The reaction of $[CpNiCO]_2$ with $AlBr_3$ to produce the nickel trimer parallels the foramtion of a Cp_3Ni_3 moiety from $[CpNiCO]_2$ by thermolysis[13,33] (see Experimental Section), by metal reduction,[13,34] or by reaction with nucleophiles.[35,36] The fact that both nucleophiles and electrophiles promote the formation of trimeric nickel compounds from the dimer suggests that this process might be especially favored by a DA surface. The various IR bands for alumina mask possible IR bands of the adsorbed trimer so no decision can be made on its presence. It is more difficult to rationalize the decomposition of the $Cp_3Ni_3(CO)_2$ adducts simply because little is known about the chemistry of the parent compound. The DA adduct is the least stable adduct formed by the trimer in this study. This suggests that the nucleophilicty of the substituent bound to the aluminum, rather than the Lewis acidity of the aluminum compound, is the factor responsible for the decomposition. These results for the nickel complexes can be compared to a preliminary report of their interaction with a silica surface.[37] Hydroxylated silica shows no Lewis acid or base properties and mild Brønsted acidity.[24] Decomposition of the nickel complexes on silica required 80–120 °C and resulted in stoichiometric production of carbon monoxide and cyclopentadiene.[37] Similar interactions have been proposed for the ethylene oligomerization catalyst prepared from $Cp_3Ni_3(CO)_2$ and a hydroxylated silica–alumina surface.[38]

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Registry No. $[CpNiCO]_2$, 12170-92-2; $Cp_3Ni_3(CO)_2$, 12194-69-3; $[CpFeCO]_4$, 12203-87-1; γ-Al_2O_3, 1344-28-1; $AlBr_3$, 7727-15-3.

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Oxidation of Dodecamethylcyclohexasilane by *m*-Chloroperbenzoic Acid

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Oxidation of dodecamethylcyclohexasilane (I) by *m*-chloroperbenzoic acid leads to six oxidation products that possess respectively one, two, three, four, five, and finally six oxygen atoms as well as all of the atoms originally present in I. The structures of these products as well as their formation are discussed.

The oxidation of silicon–silicon single bonds of disilanes by peracids,[1–9] tertiary amine oxides,[2,10] nitrogen oxides,[16] ozone,[17] sulfoxides,[11–13] and peroxides[4–7,14] as well as by molecular oxygen in both the singlet[15] and triplet[5,14] states to yield disiloxanes has been reported. On the other hand, much less work has been presented on the oxidation of silicon–silicon single bonds of polysilanes. The air oxidation of octamethylcyclotetrasilane to yield 1-oxa-2,2,3,3,4,4,5,5-octamethyl-2,3,4,5-tetrasilacyclopentane[18] and the recent report of the peracid oxidation of various 1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetramethylcyclotetrasilane isomers[9] are among the few previous results in this area.

We have been interested in the oxidation of silicon–silicon single bonds[8,11–13] and would like to report our work on the reactions of *m*-chloroperbenzoic acid (MCPBA) with dodecamethylcyclohexasilane (I). Oxidation of 1 equiv of I with 2 equiv of MCPBA leads to formation of six oxidation products as well as significant amounts (~60%) of unreacted I. These possess respectively one, two, three, four, five, and finally six oxygen atoms as well as all of the atoms originally present in I. These products may result from the sequential insertion of oxygen atoms into the silicon–silicon single bonds of I.

There are a number of possible isomeric monocyclic compounds that possess a framework of six silicon and from one to six oxygen atoms. For example, there are three isomers that possess a framework skeleton of six silicon and three oxygen atoms. Likewise, there are three isomeric compounds that have six silicon and two oxygen atoms as well as three isomers that possess four oxygen and six

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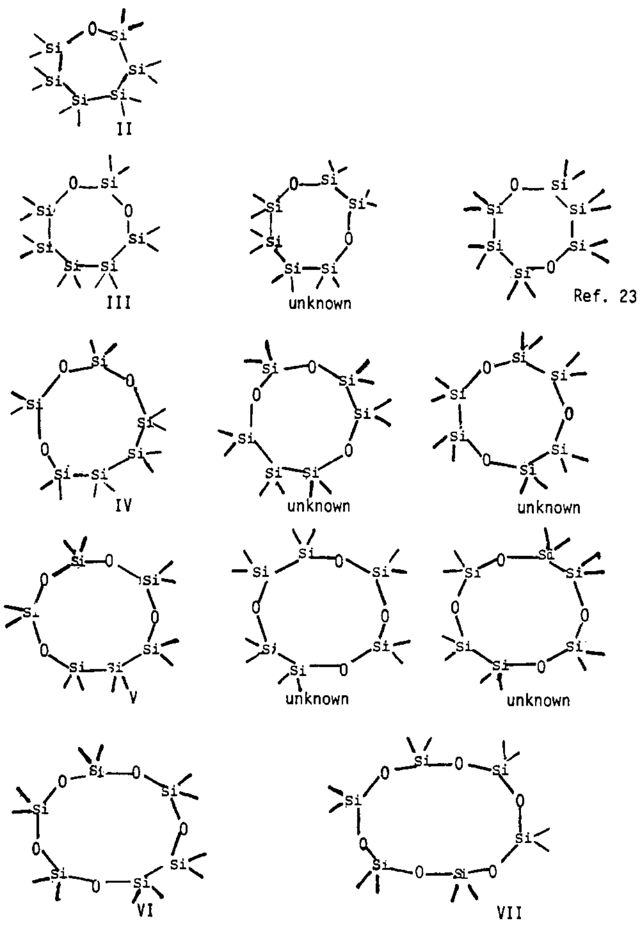
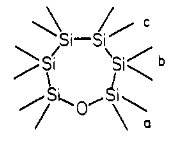


Figure 1. Oxidation products.

silicon atoms. On the other hand, there is only a single isomer that possesses one oxygen and six silicon atoms. In addition there is only a single isomer possible that possesses five oxygen and six silicon atoms as well as only one that has a six oxygen and six silicon atom framework. The possible structures of isomeric oxidations are outlined in Figure 1. Despite these numerous possible isomers, only a single isomer for each oxidation level was found. Their structures were determined by a combination of ^{1}H and ^{13}C NMR, UV, IR, and mass spectrometry and chemical analysis. For NMR data see Chart I. These have been shown to be 2,2,3,3,4,4,5,5,6,6,7,7-dodecamethyl-1-oxa-2,3,4,5,6,7-hexasilacycloheptane (II), 2,2,4,4,5,5,6,6,7,7,-8,8-dodecamethyl-1,3-dioxa-2,4,5,6,7,8-hexasilacyclooctane (III), 2,2,4,4,6,6,7,7,8,8,9,9-dodecamethyl-1,3,5-trioxa-2,4,6,7,8,9-hexasilacyclononane (IV), 2,2,4,4,6,6,8,8,9,9,-10,10-dodecamethyl-1,3,5,7-tetraoxa-2,4,6,8,9,10-hexasilacyclodecane (V), 2,2,4,4,6,6,8,8,10,10,11,11-dodecamethyl-1,3,5,7,9-pentaoxa-2,4,6,8,10,11-hexasilacycloundecane (VI), and finally 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyl-1,3,5,7,9,11-hexaoxa-2,4,6,8,10,12-hexasilacyclododecane (VII). Consistent with these structures we find a linear correlation between the number of silicon atoms in the polysilane portion of the oxidized products II, III, IV and V and the wavelength of the lowest energy transitions.[19,20] See Figure 2.

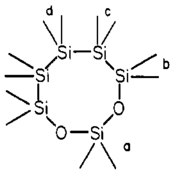
Certainly silicon–silicon single bonds adjacent to oxygen are significantly more reactive to oxidation than those that are not bonded to oxygen. A similar reactivity pattern was

Chart I. ^{1}H and ^{13}C NMR (δ) Chemical Shifts for Oxidation Products II-VII



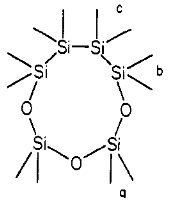
II

	a	b	c
^{1}H	0.06	0.105	0.14
^{13}C	−6.28	−5.99	2.62



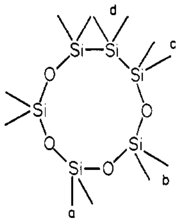
III

a	b	c	d
−0.02	0.083	0.162	0.125
−5.83	−6.202	1.39	2.234



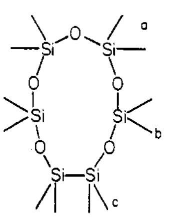
IV

	a	b	c
^{1}H	0.00	0.09	0.19
^{13}C	−6.096	1.342	2.466



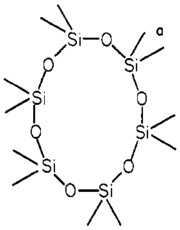
V

a	b	c	d
0.064	0.060	0.242	0.093
−6.851	1.293	2.393	0.897



VI

	a	b	c
^{1}H	0.025	0.025	0.150
^{13}C	0.96	1.269	1.688



VII

a
0.063
0.956

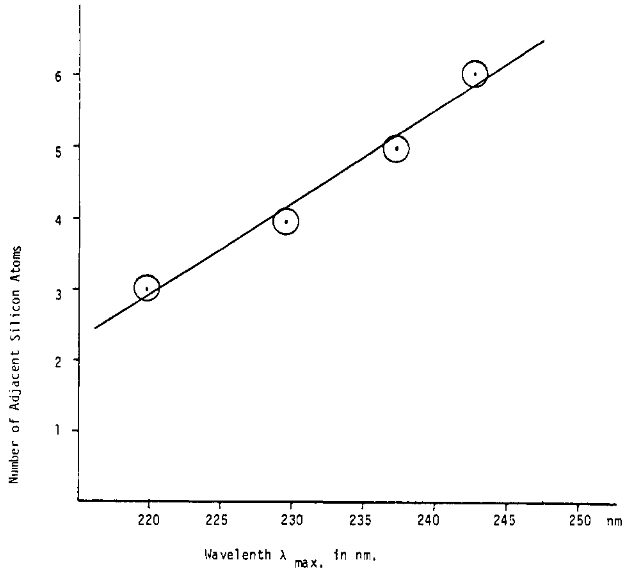


Figure 2. Correlation of λ_{max} vs. number of adjacent silicon atoms in oxidation products II–V.

found by West in the peracid oxidation of 1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetramethyltetrasilacyclobutane.[9] This may be an electronic effect as suggested by West[9] or may be due to hydrogen bonding of the peracid to the siloxane oxygen—which brings the peracid into close proximity to the adjacent silicon–silicon single bonds. Further it should

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be noted that I is significantly less reactive toward peracid oxidation than the intermediate oxidation products II–VI which possess siloxane bonds. Thus the amount of monooxidation product is lower than that of the di oxidation product, which in turn is less than that of the tri oxidation product, and so on. Further oxidation of the initially oxidation products is clearly favored. This is quite different than the result observed by West, who found that initial oxidation of the four-membered ring by peracid was favored over further oxidation.[9] This apparent acceleration of the initial oxidation in West's case probably reflects the strain of the four-membered ring rather than the inherent ease of oxidation of silicon–silicon bonds of polysilanes compared to silicon–silicon single bonds adjacent to oxygen. Of the possible cyclic isomeric oxidation products only VII[21,22] and 2,2,3,3,4,4,6,6,7,7,8,8-dodecamethyl-1,5-dioxa-2,3,4,6,7,8-hexasilacyclooctane[23] have been previously reported. There are still five oxidation products, one with two oxygens, two with three oxygens, and two with four oxygens, which are still unknown. Finally, we have found that VI undergoes facile thermal elimination of hexamethylcyclotrisiloxane and formation of 2,2,4,4,5,5-hexamethyl-1,3-dioxa-2,4,5-trisilacyclopentane. The thermal and photochemical reactions of these products are under active investigation.

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen. ^{1}H NMR spectra were recorded on a Varian XL-100 or a XL-200 spectrometer operating in the FT mode. Five percent solutions in deuteriochloroform with an internal standard of chloroform were used. ^{13}C NMR spectra were obtained on a Varian XL-200 using 10–15% solution in deuteriochloroform. ^{13}C spectra were run with broad-band proton decoupling or with off-resonance decoupling to determine the multiplicity. IR spectra were obtained on a Perkin-Elmer 281 spectrometer in $CHCl_3$ solution. Low-resolution mass spectra were obtained on a Hewlett-Packard 5985 GC–MS at an ionizing voltage of 70 eV. A 20 in. × 0.125 in. 2% OV-101 on 100/120 mesh Chromosorb W column was used in the gas chromatograph inlet of the mass spectrometer. High-resolution mass spectra were obtained on an A.E.I. MS-902 at 70 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene. GPLC analysis was performed on a Hewlett-Packard F&M 700 using a 4 ft × 0.25 in. 20% SE-30 on 60–80 mesh Chromosorb W column. There were carried out in a temperature programming mode starting at 100 °C. The temperature was increased at a rate of 2°/min. UV spectra were obtained on a Hewlett-Packard 8450 spectrometer. Spectroquality cyclohexane was used as the solvent for UV. Yields of products are calculated on the basis of recovered starting materials (65%). Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN. Dodecamethylcyclohexasilane[24,25] was prepared by reaction of dichlorodimethylsilane and lithium in tetrahydrofuran.[26] *m*-Chloroperbenzoic acid (MCPBA 85%) was obtained from Aldrich and used without further purification.

Oxidation of Dodecamethylcyclohexasilane with *m*-Chloroperbenzoic Acid. In a 100-mL round flask equipped with a Teflon covered magnetic stirring bar and a nitrogen inlet were placed 2.4 g (7.0 mmol) of dodecamethylcyclohexasilane, 50 mL of anhydrous methylene chloride, and 2.8 g (14.0 mmole) of 85% MCPBA. The mixture was stirred. *m*-Chlorobenzoic acid precipitated as the reaction proceeded. After 3 days the solution was filtered to remove *m*-chlorobenzoic acid and the reaction mixture was washed three times with aqueous sodium bicarbonate and once with water and finally dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure. GPLC analysis of the residue indicated the formation of six products. These are apparently favored by sequential insertion of oxygen into the silicon–silicon bonds of dodecamethylcyclohexasilane. Thus the first one containing one oxygen atom while the last possesses six oxygen atoms. The spectra properties and analytical data of these compounds follows. The monooxidation product was identified as 2,2,3,3,4,4,5,5,6,6,7,7-dodecamethyl-1-oxa-2,3,4,5,6,7-hexasilacycloheptane (II) (3.73% yield). It has the following properties: mp 144–146 °C ^{1}H NMR δ 0.06 (s, 12 H), 0.105 (s, 12 H), 0.14 (s, 12 H); ^{13}C NMR δ −6.280 (q), −5.991 (q), 2.620 (q); IR $\bar{\nu}$ 1040 cm^{-1} (Si–O–Si); UV λ_{max} (cyclohexane) 242.5 (ϵ 5203), 215.5 nm (14959); MS, *m/e* (relative intensity) 364 (15.9, M$^{+\cdot}$), 349 (30.5, M^{+} − 15), 291 (17.1, M − 73), 233 (12.2), 131 (11.0), 116 (39.0), 74 (11.0), 73 (100). Exact mass for $Si_6C_{12}H_{36}O$: 364.1404. Calcd: 364.1381, deviation 6.3 ppm.

The dioxidation product was shown to be 2,2,4,4,5,5,6,6,7,7,8,8-dodecamethyl-1,3-dioxa-2,4,5,6,7,8-hexasilacyclooctane (III) (7.45% yield). It has the following properties: mp 106–108 °C; ^{1}H NMR δ −0.02 (s, 6 H), 0.083 (s, 12 H), 0.125 (s, 6 H), 0.162 (s, 12 H); ^{13}C NMR δ −6.202 (q), −5.830 (q), 1.390 (q), 2.234 (q); IR $\bar{\nu}$ 1030 cm^{-1} (Si–O–Si); UV λ_{max} (cyclohexane) 237.2 (ϵ 7680), 217.3 nm (15675.6); MS, *m/e* (relative intensity) 380 (15.1, M$^{+\cdot}$), 365 (22.6, M^{+} − 15), 307 (57, M − 73), 249 (14.0), 131 (12.9), 116 (34.4), 74 (10.8), 73 (100); exact mass for $Si_6C_{12}H_{36}O_2$: 380.1337. Calcd: 380.1331, deviation 1.5 ppm. Anal. Calcd for $Si_6C_{12}H_{36}O_2$: C, 37.93; H, 9.55. Found: C, 38.14; H, 9.53.

The trioxidation product was found to be 2,2,4,4,6,6,7,7,8,8,9,9-dodecamethyl-1,3,5-trioxa-2,4,6,7,8,9-hexasilacyclononane (IV) (25.6% yield). It has the following properties: mp 45–47 °C (glassy, semisolid); ^{1}H NMR δ 0.00 (s, 12 H), 0.09 (s, 12 H), 0.19 (s, 12 H); ^{13}C NMR δ −6.096 (q), 1.342 (q), 2.466 (q); IR $\bar{\nu}$ 1070 cm^{-1} (Si–O–Si); UV λ_{max} (cyclohexane) 229.5 (ϵ 6576.5), 209 nm (13513.5); MS, *m/e* (relative intensity) 396 (9.3, M$^{+\cdot}$), 381 (17.8, M^{+} − 15), 323 (45.0, M − 73), 265 (8.1), 174 (21.7), 131 (16.3), 116 (29.1), 74 (7.4), 73 (100). Exact mass for $Si_6C_{12}H_{36}O_3$: 396.1287. Calcd: 396.1280, deviation 1.7 ppm. Anal. Calcd for $Si_6C_{12}H_{36}O_3$: C, 36.40; H, 9.16. Found: C, 36.09; H, 9.10.

The tetraoxidation product was identified as 2,2,4,4,6,6,8,8,9,9,10,10-dodecamethyl-1,3,5,7-tetraoxa-2,4,6,8,9,10-hexasilacyclodecane (V) (15.4% yield). It has the following properties: ^{1}H NMR δ 0.060 (s, 12 H), 0.064 (s, 6 H), 0.093 (s, 6 H), 0.242 (s, 12 H); ^{13}C NMR δ −6.851 (q), 0.895 (q), 1.293 (q), 2.393 (q); IR $\bar{\nu}$ 1065–1075 cm^{-1} (Si–O–Si); UV λ_{max} (cyclohexane) 220 nm (ϵ 9078); MS, *m/e* (relative intensity) 412 (1.2, M$^{+\cdot}$), 397 (8.5, M^{+} − 15), 339 (7.9, M − 73), 309 (8.6), 281 (7.9), 207 (11.5), 116 (100), 73 (69). Exact mass for $Si_6C_{12}H_{36}O_4$: 412.1226. Calcd: 412.1230, deviation 0.9 ppm. Anal. Calcd for $Si_6C_{12}H_{36}O_4$: C, 34.98; H, 8.81. Found: C, 35.07; H, 8.93.

The pentaoxidation product 2,2,4,4,6,6,8,8,10,10,11,11-dodecamethyl-1,3,5,7,9-pentaoxa-2,4,6,8,10,11-hexasilacycloundecane (VI) (22.07% yield) was obtained and has the following properties: ^{1}H NMR δ 0.025 (s, 24 H), 0.150 (s, 12 H); ^{13}C NMR δ 0.960 (q), 1.269 (q), 1.688 (q); IR $\bar{\nu}$ 1065–1070 cm^{-1} (Si–O–Si); MS, *m/e* (relative intensity) 428 (2.5, M$^{+\cdot}$), 413 (9.6, M^{+} − 15), 355 (13.2, M − 73), 325 (10.4), 267 (14.0), 206 (14.7), 191 (15.7), 147 (12.4), 131 (18.0), 73 (100). Exact mass for $Si_6C_{12}H_{36}O_5$: 428.1177. Calcd: 428.1178, deviation 0.2 ppm.

The final product dodecamethylcyclohexasiloxane[21] (VII) (25.7% yield) was formed and has the following properties: ^{1}H NMR δ 0.063 (s, 36 H); ^{13}C NMR δ 0.956 (q); IR $\bar{\nu}$ 1060–1090 cm^{-1} (Si–O–Si); MS, *m/e* (relative intensity) 429 (33.0, M^{+} − 15), 341 (67.0), 325 (20.8), 147 (11.5), 73 (100).

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Registry No. I, 4098-30-0; II, 85294-07-1; III, 85294-08-2; IV, 85294-09-3; V, 85304-56-9; VI, 85294-10-6; VII, 540-97-6; MCPBA, 937-14-4.

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