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SYNTHESIS AND THERMOCHEMISTRY OF 4-DIAZO-1,1-DIMETHYL-1-SILACYCLOHEXA-2,5-DIENE

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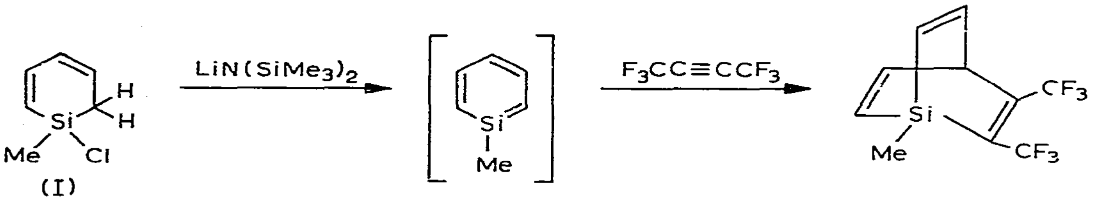
Summary

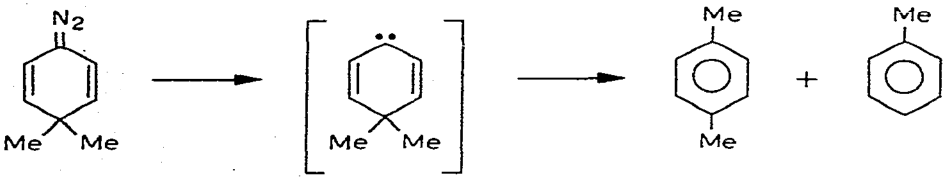
A vastly improved synthesis of 1,1-dimethyl-1-silacyclohexa-2,5-diene-4-one is described. Direct conversion of the ketone to the diazo derivative is easily accomplished, but a simpler method, not involving the ketone, is presented for synthesis of the title compound. In an attempt to observe rearrangement of the diazo system, pyrolysis under a variety of techniques was performed. No evidence of formation of a silabenzene was obtained.

Recently we presented evidence [1] for the transient intermediacy of a silabenzene in the reaction of chlorosilane I with base in the presence of an acetylene trap. Since this method suffers from complexity of the product mixture and the existence of an alternate two-step mechanism, we have continued our search for a less ambiguous method of silabenzene generation.



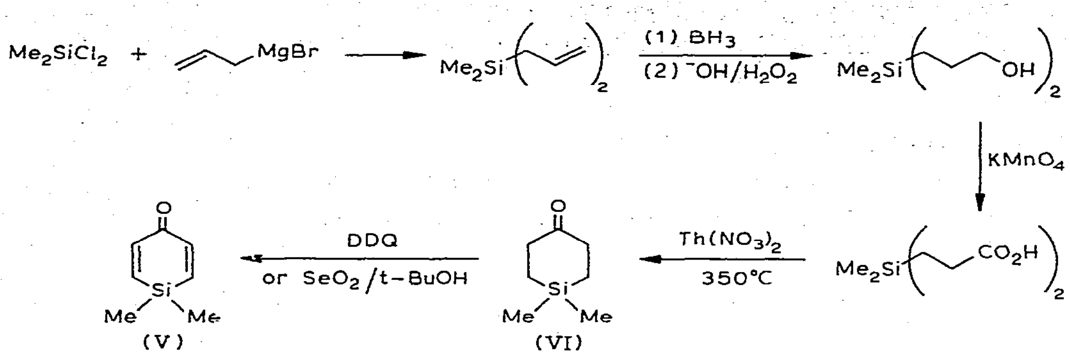
(I)

For some years it has been known that the gas-phase thermolysis of diazocyclo hexadiene II affords *p*-xylene and toluene [2]. Thus it was hoped that an analo-



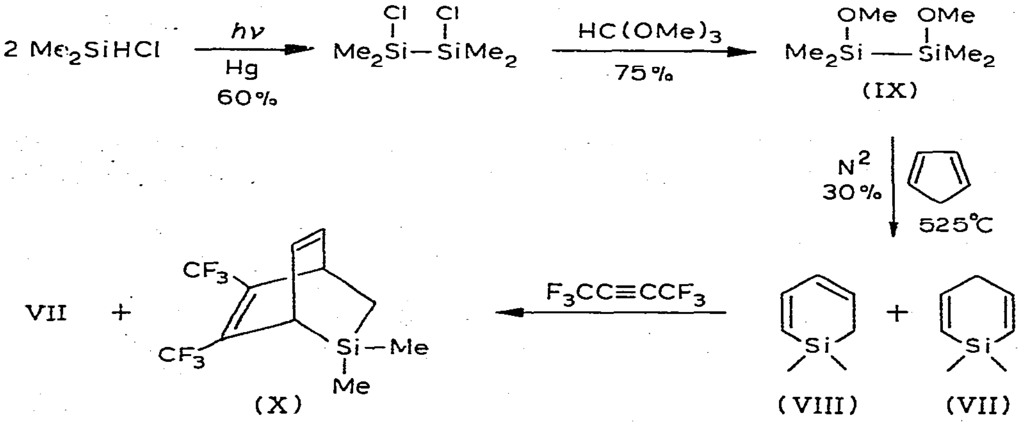
(II) (III)

gous rearrangement would occur upon replacement of the methyl-substituted carbon of 1,1-dimethylcyclohexadienylidene (III) with silicon. The immediate precursor, 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene (IV) was not known, but the corresponding ketone V had been reported [3,4]. The literature preparation of V involved the tedious synthesis of the saturated ketone VI followed by dehydrogenation to V. The last step in this sequence, oxidation of VI to V, proved to be troublesome in our hands. This oxidation is reported to occur



through the use of selenium dioxide/t-butyl alcohol [3] or 2,3-dichloro-5,6-dicyanoquinone (DDQ) [4]. Indeed we found that reaction of VI with SeO_2 did produce dienone V, but the purification of the dienone away from foul-smelling organoselenium by-products was extremely tedious and resulted in considerably decreased isolated yields (ca. 15%). Treatment of VI with DDQ is reported to afford the dienone in 62% yield in a much cleaner reaction. However, in our hands numerous attempts with varying reaction conditions produced at best only traces of V. Thus, it became obvious that an alternative synthesis of dienone V was necessary to obtain workable amounts of this compound.

The problem of introduction of the double bonds in the silacyclohexanone ring system was circumvented by beginning with the double bonds already present and introducing the ketone functionality in the final step. The key compound in our scheme is 1,1-dimethyl-1-silacyclohexa-2,5-diene (VII) which can be obtained [5] along with the isomeric VIII from the gas-phase copryrolysis of 1,1,2,2-tetramethyl-1,2-dimethoxydisilane (IX) and cyclopentadiene.



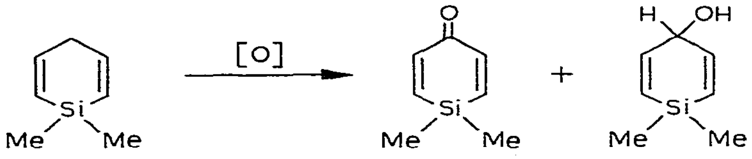
Separation of the isomeric dienes VII and VIII proved difficult as chromatographic attempts to cleanly separate the mixture failed. The isomers were separated by treating the mixture with perfluoro-2-butyne in a sealed tube at 60°C for 4 h. The conjugated isomer VIII is thus removed as Diels—Alder adduct X as previously described [6].

The synthesis of dimethoxydisilane IX merits mention since it differs from previously reported methods [7]. Synthesis of tetramethyl-1,2-dichlorodisilane by treatment of hexamethyldisilane with acetyl chloride and aluminum chloride yields a mixture of chlorodisilanes which requires tedious distillations for separation. We find that 1,2-dichlorotetramethyldisilane is more conveniently prepared by the mercury sensitized photolysis of chloromethyldimethylsilane. This reaction is modeled after the coupling of dimethoxymethylsilane reported by Childs and Weber [8]. After two days of irradiation, the dichlorodisilane is obtained in 60% yield and free from contamination by other chlorodisilanes. Conversion to IX was accomplished with trimethylorthoformate [8] and the product purified by simple distillation.

Oxidation of VII to ketone V was accomplished with a variety of oxidizing agents. Treatment of diene VII with selenium dioxide in refluxing 95% ethanol for 24 h afforded V in 10% isolated yield along with an equal amount of alcohol XI. Also accompanying the products were large amounts of unidentified organoselenium by-products. This oxidation suffered from the same purification problems as were experienced with the SeO_2 oxidation of ketone VI.

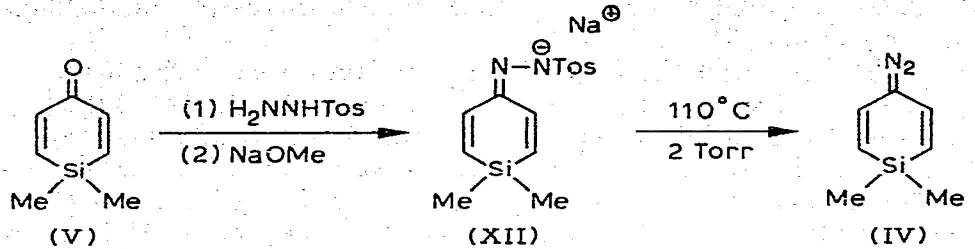
Collin's reagent ($CrO_3 \cdot 2$ Py) [9] transformed VII to V in 30% yield. No XI was found among the products, but a considerable quantity of unidentified acids was obtained, presumably arising from ring opening.

Activated manganese dioxide was found to be a milder and thus superior oxidizing agent. Conversion to V occurred in 30% yield simply through stirring at room temperature in hydrocarbon solvent for 24 h. Purification involved only chromatography on silica gel. Furthermore, it was later found that this oxidation could be carried out in the presence of conjugated diene VIII, making separation of the isomeric diene mixture no longer necessary. The conjugated isomer (VIII) was untouched by MnO_2 and could be isolated by chromatography. This was not the case with oxidation by SeO_2 or Collin's reagent where no trace either of VIII or the corresponding ketone could be found. The overall isolated yield of V, starting from commercially available dimethylchlorosilane, is about 5% in four steps.

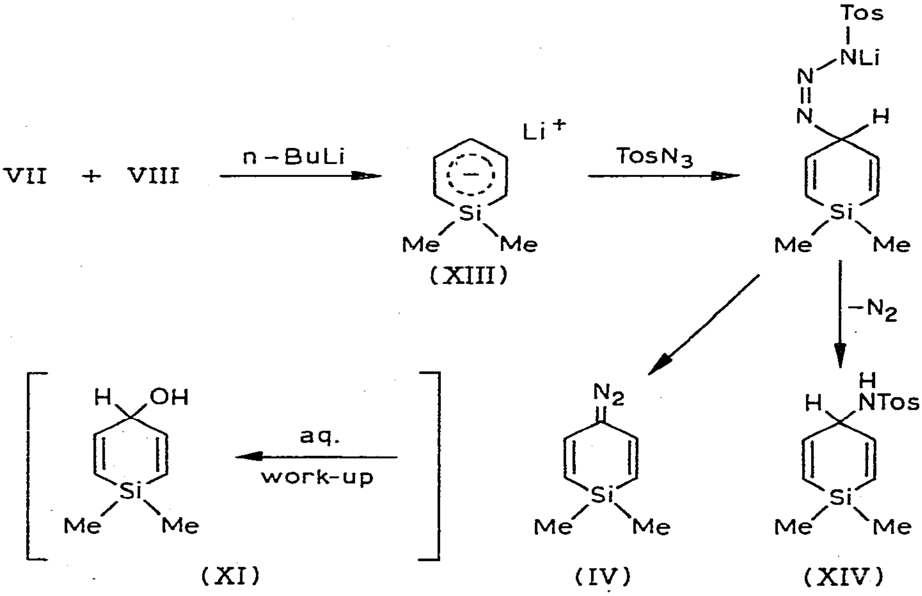


(VII)		(V)	(XI)
	SeO_2	10%	10%
	$CrO_3 \cdot 2Py$	30%	—
	MnO_2	30%	—

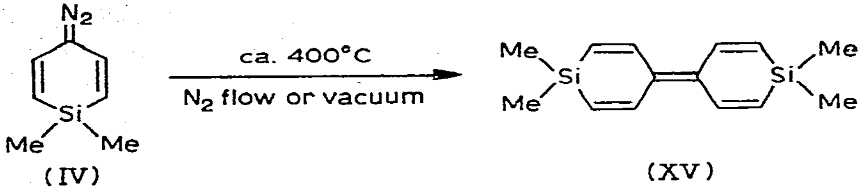
Conversion of V to the desired diazo compound IV was accomplished by standard procedures. Thus, treatment of V with *p*-toluenesulfonyl hydrazide afforded the white, crystalline tosylhydrazone which was treated with sodium methoxide to produce the sodium salt XII. Pyrolysis of XII at 110°C (2 Torr) afforded the red, liquid IV in 70% yield.



During the course of this study, the metallation of VII with n-butyllithium was reported by Chernyshev [10]. This suggested that a direct route to IV might be available through the diazo transfer reaction first reported by Doering and DePuy [11]. Thus a mixture of dienes VII and VIII was treated with n-butyllithium in THF at 0°C. The red silacyclohexadienyl anion XIII was formed immediately. Addition of the anion solution to a solution of *p*-toluenesulfonyl azide in THF at —77°C produced, upon workup, IV in 44% yield, 10% of alcohol XI (shown to result from the aqueous workup of IV), and variable amounts of amide XIV.

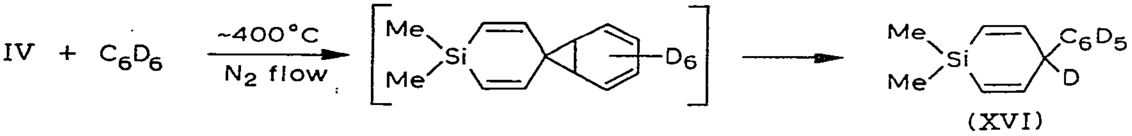


Decomposition of diazo compound IV was performed in the gas phase at ca. 400°C in a vertical flow pyrolysis apparatus. The sample was introduced either by syringing microliter quantities through a septum or by slow evaporation with a stream of nitrogen into the heated tube to insure conditions of maximum dilution. The pyrolysis produced a complex product mixture of which the only identifiable product was dimer XV. Dimer XV could easily be distinguished from various 2 + 2 and 2 + 4 silaxylene dimer possibilities from its classic symmetrical AB pattern in the olefinic region of its NMR spectrum. In an attempt

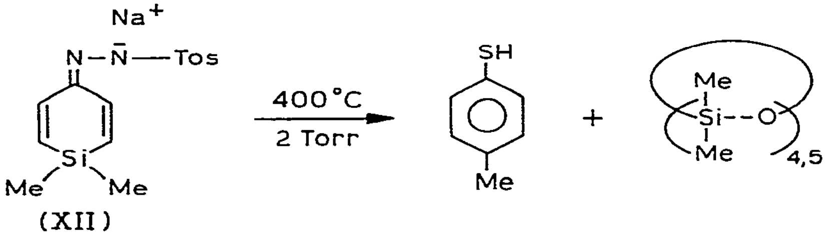


to increase dilution, a standard, horizontal vacuum pyrolysis of IV was tried. Slow distillation of IV (0.15 Torr) through a hot zone of 420°C afforded a product mixture containing ca. 5% of XV along with a large amount of non-volatile polymers. Again, no evidence for the formation of a silabenzene was found.

In another attempt to promote intramolecular rearrangement of the carbene, a dilute solution of IV (0.01 *M*) in benzene-d_6 was pyrolyzed in a nitrogen flow system (ca. 400°C). The product mixture was much cleaner with only one major volatile product being observed. Unfortunately, the product was simply an adduct of the carbene and solvent (presumably structure XVI). Similar behavior has been reported for the photolytically generated carbon analog III [12], which proceeds through the intermediacy of the thermally unstable norcaradiene form.



Since direct thermal decomposition of the lithium salt of the tosylhydrazone of 4,4-dimethylcyclohexa-2,5-dien-1-one has also been reported [2] to produce xylene, it was hoped that this method would produce an analogous rearrangement when applied to XII. Thus, the sodium salt XII was slowly dropped onto a glass surface heated to 400°C under vacuum. The major silicon-containing volatile products were, surprisingly, octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5). The only other identifiable product was *p*-methylthiophenol. A large amount of intractable tar was also formed. Although we find that the sodium salt of tosylhydrazide itself produces this thiophenol under these reaction conditions, we are at a loss to explain our surprising results with XII.



Since all logical methods of thermal generation of the desired carbene have been explored, we must conclude that once again [13] the conceptionally minor modification of replacement of a single carbon atom by its neighbor, silicon, produces drastic changes in the thermal chemistry of the system. It is difficult not to ascribe at least some of the blame to the inherent instability of $(p-p)\pi$ bonded silicon.

Experimental

Routine proton NMR spectra were recorded either on a Varian model A-60, EM-360, or a Hitachi R20-B spectrometer. A Varian HA-100 spectrometer was used to record all 100 MHz spectra. Decoupling experiments were performed either on the Varian EM-360 or HA-100 spectrometer. All chemical shifts were reported as parts per million (δ scale) using either tetramethylsilane or chloroform as internal standards.

^{13}C NMR spectra were recorded on a Bruker HX-90 NMR spectrometer equipped with a Nicollet 1089 data system.

Infrared (IR) spectra were recorded on either a Beckman IR-4250 or a Beckman Acculab-2 infrared spectrophotometer. All bands are reported in reciprocal centimeters (cm^{-1})

Routine mass spectra were recorded on an Atlas CH-4 mass spectrometer. Exact mass measurements were obtained on a MS-902 mass spectrometer. Gas chromatographic mass spectra (GCMS) were obtained on either a Perkin—Elmer 270 mass spectrometer or a Finnegan Model 4023 mass spectrometer.

Ultraviolet spectra (UV) were recorded on a Cary Model 14 spectrophotometer. All melting points (m.p.) were obtained on a Thomas—Hoover capillary melting point apparatus and are uncorrected. Gas chromatographic (GC) data were obtained on a Varian-Aerograph Series 1700 gas chromatograph. High pressure liquid chromatography (HPLC) was performed on a Waters high pressure liquid chromatograph equipped with UV and differential refractometer detectors.

Standard procedures for flow pyrolysis

A vertical tube (17 mm × 30 cm) was packed with Vycor chips and prepurified nitrogen was passed through the tube. A liquid nitrogen-cooled trap was used to collect the pyrolysate. Samples to be pyrolyzed, either neat or as solutions, were dropped directly into the heated tube and allowed to collect in the cold traps.

Synthesis of 1,1-dimethyl-1-silacyclohexan-4-one (VI)

The procedures of Benkeser and Bennett [14] and of Weber and coworkers [3] were followed to prepare this yellow oil, b.p. 46°C (1.0 Torr) (mol. wt. 129), in 2—3% overall yield: NMR (CCl_4) δ 0.13 (s, 6H), 0.88 (t, 4H, J 7.5 Hz), 2.40 (t, 4H, J 7.5 Hz); IR (liquid film) 3120, 1675, 1250, and 780 cm^{-1}.

Selenium dioxide oxidation of VI to 4,4-dimethyl-4-silacyclohexa-2,5-diene-1-one (V) in t-butyl alcohol

The procedure of Weber and Laine [3] was followed. The yellow oil was obtained in 15% isolated yield: NMR ($CDCl_3$) δ 0.20 (s, 6H), 6.87 (center d of d, 4H, J 14.5 Hz); IR (film) 1635, 1580 cm^{-1}; mass spectrum (16 eV) m/e (rel. intensity) 138 (24), 125 (33), 110 (100), 95 (28).

Attempted oxidation of VI with DDQ

The procedure of Felix and Weber [4] was followed. In our hands the reaction did not produce dienone IV. Extension of reaction times, change of solvent to methylene chloride, toluene, or xylene did not alter the results. Freshly preparing the DDQ also had no effect on the reaction. In all cases, starting material VI and a small amount of uncharacterized silicon polymer were obtained.

Mercury photosensitized coupling of dimethylchlorosilane

In a dry 500 ml quartz tube, was placed 217 g (2.29 mol) of dimethylchlorosilane boiling chips, and a drop of mercury. Nitrogen was passed through the liquid for thirty minutes prior to photolysis. The tube was equipped with two condensers and placed under a N_2 atmosphere. Photolysis was accomplished in a Rayonet reactor with 2537 Å light for two days. Distillation yielded 125 g (0.67 mol) (58% yield) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, b.p. 143—146°C (760 Torr): NMR (CCl_4) δ 1.0 (65); mass spectrum (70 eV) *m/e* (rel. intensity) 186 (9), 151 (15), 93 (95), 73 (100), 58 (95).

Synthesis of 1,1,2,2-tetramethyl-1,2-dimethoxysilane (IX)

In a dry 500 ml flask, equipped with a magnetic stirring bar, condenser, and $CaCl_2$ drying tube, was placed 260 g (1.39 mol) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane and 738 g (6.96 mol) of trimethylorthoformate. This mixture was heated at 60°C for 12 h. Distillation of the reaction mixture yielded 185 g (1.04 mol) (75% yield) of 1,1,2,2-tetramethyl-1,2-dimethoxydisilane IX boiling in the range 138—151°C (760 Torr). NMR (CCl_4) δ 0.2 (s, 2H), 3.36 (s, 1H); mass spectrum (70 eV) *m/e* (rel. intensity) 178 (86), 148 (100), 118 (18).

Preparation of 1,1-dimethyl-1-silacyclohexa-2,4- and-2,5-diene (VIII and VII)

One equivalent of 1,1,2,2-tetramethyl-1,2-dimethoxydisilane (IX) was mixed with three equivalents of cyclopentadiene and dropped into a 12" × 3/4" Vycor tube packed with quartz chips, swept with nitrogen, and heated to 520—550°C. The product was collected in a liquid nitrogen cooled-flask and immediately fractionally distilled to prevent dimerization of the excess cyclopentadiene. A 35—40% yield of a mixture of the 2,5- and 2,4-silacyclohexadienes was obtained, b.p. 125—129°C (760 Torr). This fraction was filtered through silica gel with hexane as a final purification procedure. At 520°C, the mixture consisted of 2.5 parts 2,4-diene to 1 part 2,5-diene. Higher temperatures favored the conjugated isomer. The isomers could not be separated by GC on 15% SE-30, 20% DC-550, 10% Carbowax 20M, or 5% Dexsil 300, nor were they separated by HPLC on 1 ft. μ-Porasil or 1 ft. μ-Bondapak. 1,1-Dimethyl-1-silacyclohexa-1,5-diene (VII): NMR (CCl_4) δ 0.10 (s, 6H), 2.89 (center of sym. d, 2H), 5.57—6.05 (unsym. m, 2H), 6.45—6.95 (unsym. m, 2H); IR (film) 2980, 1655, 1607, 1375, 1245; ^{13}C NMR 144.9 (2C), 126.2 (2C), 33.9 (1C), —0.34 (1C); mass spectrum (70 eV) *m/e* (rel. intensity) 124 (80), 109(100), 93 (10), 81 (35); exact mass calculated for $C_7H_{12}Si$, *m/e* 124.0708; found: *m/e* 124.0706 ± 0.0005. 1,1-Dimethyl-1-silacyclohexa-2,4-diene (VIII): NMR (CCl_4) δ 0.12 (s, 6H), 1.45 (d, 2H, *J* 3.5 Hz), 5.75—6.2 (m, 2H), 6.5—7 (m, 2H); mass spectrum (70 eV) *m/e* (rel. intensity) 124 (30), 109 (100), 81 (29).

Purification of 1,1-dimethyl-1-silacyclohexa-2,5-diene (VII)

A mixture of 2.4 parts VIII and 1 part VII was treated with excess perfluoro-2-butyne in an evacuated, degassed sealed tube at 60°C according to the procedure of Barton and Kline (VI). The 2,5-silacyclohexadiene (VII) was untouched and recovered pure by distillation b.p. 65—67°C (48 Torr). The product of the Diels—Alder reaction 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]-octa-2,5-diene (X) distilled at 78—80°C (14 Torr): NMR (CCl_4) δ 0.11 (s, 6H), 0.48 (d, 2H, J 3.8 Hz), 3.58 (d, 1H, 6.5 Hz), 4.12 (m, 1H), 6.16 (m, 2H).

Oxidation of VII by selenium dioxide

To a refluxing solution of 2.32 g (0.018 M) of VII in 50 ml of 95% ethanol was added, dropwise over a 3 h period, a solution of 2.0 g (0.18 mol) of selenium dioxide in 50 ml of 95% ethanol. The reaction mixture was refluxed an additional 2 h, after which time most of the ethanol (80—90 ml) was distilled from the reaction vessel. The mixture was cooled, diluted with 100 ml of 95/5 pentane/chloroform, and filtered. The red-brown solution was washed three times with 75 ml of water and once with saturated NaCl and dried over anhydrous $MgSO_4$. Filtration and removal of solvent yielded 1.97 g of a dark red oil. The oil was purified by column chromatography on silica gel. Elution with 95/5 hexane/diethyl ether produced 0.252 g (0.0018 mol) of pure 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one (V, 10.1% isolated yield). Elution with 90/10 hexane/diethyl ether gave 0.262 g (0.0018 mol) (10.4% isolated yield) of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ol (XI) [14]: NMR (CCl_4) δ 0.07 (d, 6H, J 3.5 Hz), 1.8 (s, 1H, disappears with D_2O), 4.4 (m, 1H), 5.8 (center d of d, $2H_A$, J_{AB} 14.5 Hz, J 2 Hz), 6.7 (center d of d, $2H_B$, J 4 Hz); IR (film) 3320, 2980, 2960, 2900, 1640, 1618, 1583, 1410, 1370, 1247 cm^{-1}.

Collins oxidation of a mixture of VII and VIII

To a solution of 4.0 (0.032 mol) of a 2/1 mixture of VIII to VII in 50 ml of CH_2Cl_2 stirred under nitrogen at room temperature, was slowly added a solution of 35 g (0.15 mol) of Collins reagent (Chromium trioxide-pyridine complex), prepared by the method of Dauben and coworkers [9] in 100 ml of CH_2Cl_2. The reaction was followed by GC. After 15 h, no starting material could be detected. The reaction mixture was filtered through Celite. The Celite pad was washed with an additional 300 ml of CH_2Cl_2. The CH_2Cl_2 was removed and replaced with 100 ml of hexane. The hexane solution was extracted three times with 100 ml of H_2O and once with saturated NaCl, and dried over anhydrous $MgSO_4$. Filtration and removal of the hexane left a yellow oil which was purified by column chromatography on silica gel. Elution with 95/5 hexane/Et_2O yielded 1.29 g (0.0093) (29.2% isolated yield) of 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one (V).

"Activated" manganese dioxide oxidation of VII

A solution of 1.02 g (0.0065 mol) of VII in 100 ml of dry hexane was mixed with 6.1 g (0.07 mol) of activated manganese dioxide (Ventron) and stirred for 24 h. The reaction mixture was filtered through a Celite pad and the pad was washed with 300 ml of CH_2Cl_2. Removal of the solvent left a yellow oil which was purified by column chromatography on silica gel. Elution with 95/5 hexane/Et_2O yielded 0.27 g (0.0020 mol, 30.1% isolated yield) of pure dienone V.

"Activated" manganese dioxide oxidation of a mixture of VII and VIII

A mixture of 3.34 g (0.027 mol) consisting of 2 parts VIII to 1 part VII was treated with 47 g (0.05 mol) of activated manganese dioxide (Ventron) as described above. Elution with hexane from a silica gel column yielded 1.61 g of 2,4-silacyclohexadiene (VIII), and 95/5 hexane/Et_2O yielded 0.58 g of pure dienone V. The 30% yield (0.58 g) is based on the amount of diene reacted.

Formation of the tosylhydrazone of 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one

A solution of 0.100 g (0.73 mmol) of dienone V in 20 ml of dry MeOH was added slowly to a stirring suspension of 0.135 g (0.73 mmol) of tosylhydrazide in 30 ml of MeOH. The mixture was heated to dissolve the hydrazide and then allowed to sit at 0°C for 12 h, during which time tan crystals formed. These crystals were collected and recrystallized from EtOH/H_2O to yield 0.190 g (0.62 mmol) (85% yield) of tosylhydrazone, a white crystalline material, m.p. 176—178°C: NMR (acetone-d_6) δ 0.18 (s, 6H), 2.42 (s, 3H), 6.30 (center d of m, 2H), 6.91 (center d of m, 2H), 7.35 (d, 2H, J 8.5 Hz), 7.81 (d, 2H, J 8.5 Hz); mass spectrum (70 eV) *m/e* (rel. intensity) 205 (3), 151 (27), 150 (32), 122 (100), 107 (60), 96 (55), 91 (44); exact mass calculated for $C_{14}H_{18}SiN_2SO_2$, *m/e* 306.0858; found: *m/e* 306.0838 ± 0.003.

Procedure for the generation of 1,1-dimethyl-1-silacyclohexadienyl anion (XIII)

One equivalent of a 2/1 mixture of silacyclohexadienes VIII and VII was dissolved in dry THF under a nitrogen atmosphere. The solution was cooled to 0°C. One equivalent of either n-butyllithium in pentane (Aldrich) or t-butyllithium in pentane (Aldrich or Ventron) was slowly syringed through a septum into the flask. The solution turned a deep red color upon addition of a one-half equivalent of base, and remained that color after addition was complete. The red solution was allowed to stir an additional thirty minutes to insure complete anion formation. This solution was then treated with the desired reagents.

Formation of 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene (IV)

Method I. The tosylhydrazone was generated as described above from 1.04 g (7.5 mmol) of dienone V. This solution was cooled to 0°C and 0.18 g (7.5 mmol) of sodium was added to the methanol solution to generate sodium methoxide in situ. A red-orange color developed, and after 30 min the methanol was removed under vacuum. 2.16 (6.6 mmol) of a solid were obtained. This solid was used without further purification. When this solid was rapidly heated to 110—130°C under vacuum (0.2 Torr), 0.79 g (5.3 mmol) (70% yield) of a red oil were collected. The red oil was identified as 1,1-dimethyl-4-diazo-1-silacyclohexa-2,5-diene (IV): NMR ($CDCl_3$) δ 0.10 (s, 6H), 5.55 (d, 2H, J 14 Hz), 6.84 (d, 2H, J 14 Hz); IR (film), 3010, 2970, 2900, 2050, 1576, 1528, 1308, 1245 cm^{-1}; mass spectrum (70 eV) *m/e* (rel. intensity) 150 (50), 122 (100), 107 (85), 95 (90); UV λ_{max} (pentane) 2960 Å, 2130 Å; exact mass calculated for $C_7H_{10}N_2Si$, *m/e* 150.0613; found: *m/e* 150.0613.

Method II. A 2/1 mixture of dienes VIII and VII (2.14 g) (0.017 mol) was converted to anion XIII at 0°C with n-butyllithium in THF. This anion was slowly transferred by syringe to a flask cooled to −77°C which contained a THF solution of 2.8 (0.020 mol) of tosylazide in THF under nitrogen. After addition was complete, the dark brown mixture was allowed to stir for 3 h while warming to room temperature. The reaction mixture was diluted with 200 ml of pentane and extracted six times with 150 ml portions of water and once with an equal volume of saturated NaCl. The pentane solution was dried over anhydrous $MgSO_4$, filtered, and the solvent removed. The residual, red oil was purified by chromatography on silica gel. Elution with hexane gave, after solvent removal, 1.12 g (0.0075 mol) (44% isolated yield) of the 4-diazo compound IV. Elution with 90/10 hexane/Et_2O yielded, after solvent removal, 0.24 g (0.0017 mol) (10% isolated yield) of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ol (XI). Elution with 100% diethyl ether gave a 0.95 g (0.003 mol) (19% yield) red-brown oil which crystallized to tan crystals (m.p. 122—124°C), which were identified as the 4-tosylamine of 1,1-dimethyl-1-silacyclohexa-2,5-diene (XIV): NMR ($CDCl_3$) δ −0.05 (s, 3H), −0.10 (s, 3H), 2.40 (s, 3H), 4.45 (center of m, 2H), 5.81 (center d of d, 2H, J 3 Hz, J 15 Hz), 6.39 (center d of d, 2H, J 4 Hz, J 15 Hz), 7.30 (d, 2H, J 9 Hz), 7.82 (d, 2H, J 9 Hz); IR (CCl_4 soln.) 3120, 3040, 2950, 1620, 1585, 1375, 1160; mass spectrum (70 eV) *m/e* (rel. intensity) 293 (<1), 278 (10), 229 (18), 149 (35), 138 (100), 112 (20), 91 (28); exact mass calculated for $C_{14}H_{19}O_2SNSi$, *m/e* 293.0906; found: *m/e* 293.0998.

Vertical flow pyrolysis of IV

4-Diazo compound IV was pyrolyzed neat following standard pyrolysis procedures stated previously. Sample introduction was accomplished by either slowly syringing microliter quantities, through a septum, into the tube or by evaporation of IV from a reservoir suspended over the hot zone. Temperatures varied from 385—430°C. In a typical experiment, 0.70 g (0.0047 mol) of IV was slowly dropped through a tube at 420°C under nitrogen. The material condensed in cold traps weighed 0.49 g. Purification of the condensed material was accomplished by silica gel chromatography. Elution with hexane yielded 0.180 g (0.0007 mol) (15.7% yield) of a yellow, viscous oil which was identified as the dimer XV of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ylidene: NMR (CCl_4) δ 0.15 (s, 6H), 6.13 (d, 2H, J 15 Hz), 7.75 (d, 2H, J 15 Hz); mass spectrum (70 eV) *m/e* (rel. intensity) 244 (70), 229 (100), 161 (10), 160 (10), 159 (10), 145 (10), 107 (5), 73 (15); exact mass calculated for $C_{14}H_{20}Si_2$, *m/e* 244.1104; found: *m/e* 244.1100 ± 0.0007. Elution with varying ratios of hexane/ether produced 0.08 g of material bearing only methylsilicons NMR (CCl_4) δ 0.1 (broad singlet). This product was not identified further. No other material eluted from the column. If moisture was not rigorously excluded from the pyrolysis, varying amounts of 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one (V) were eluted with 90/10 hexane/Et_2O.

Vacuum pyrolysis of IV

Pyrolysis of IV at 420—450°C at 0.15 Torr was accomplished by evaporating through a stopcock small amounts of IV into a heated tube packed with Vycor chips. Products were condensed into a series of liquid nitrogen traps.

Analysis of the condensed material gave the same results as in the vertical flow pyrolysis of IV.

Vertical flow pyrolysis of IV in benzene-d_6

Pyrolysis of 0.15 g (0.001 mol) of IV in 5 ml of benzene-d_6 was accomplished in the standard fashion at 390—400°C. Bulb-to-bulb distillation yielded 0.13 g (0.00063 mol) (63% yield) of benzenecarbene adduct XVI. An analytical sample was obtained by GC on a 6 ft. by 1/4 in., 15% SE 30 on Chromosorb W column: NMR (benzene-d_6) δ 0.4 (s, 6H), 6.0 (d, 2H, J 15 Hz), 6.75 (d, 2H, J 15 Hz), 7.2 (broad signal from benzene); mass spectrum (70 eV) *m/e* (rel. intensity) 206 (60), 191 (58), 163 (14), 140 (40), 74 (60), 59 (100); Exact mass measurements: calculated for $C_{13}D_6H_{10}Si$, *m/e* 206.1400; found: 206.1344; for $Cl_2D_6H_7Si$, *m/e* 191.1163; found: *m/e* 191.1159; for $C_{10}D_2H_5Si$, *m/e* 163.0866; found: *m/e* 163.0860; for $C_5D_5H_6Si$, *m/e* 140.0944; found: *m/e* 140.0943.

Flash vacuum pyrolysis of the sodium salt of the tosylhydrazone of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-one (XII)

Onto a glass surface heated to 400°C under a vacuum of 2.0 Torr, was dropped, in small portions, 0.62 g (1.9 mmol) of salt XII. Volatile decomposition products were condensed in a series of three liquid nitrogen cold traps. The contents of the first trap (0.31 g) (61% recovered) were analyzed by mass spectroscopy without exposure to air, mass spectrum (70 eV) *m/e* (rel intensity) 335 (5), 281 (15), 207 (35), 124 (36), 91 (40), 58 (50), 43 (100); exact mass measurements calculated for $C_7H_{21}Si_4O_4$, *m/e* 281.0515; found: *m/e* 281.0522 ± 0.0014; calculated for C_7H_8S, *m/e* 124.0345; found: *m/e* 124.0348 ± 0.0006; Peaks at *m/e* 355, 281, 207 correspond to $P - 15$ peaks for the pentamer, tetramer, and trimer cyclosiloxanes. C_7H_8S is *p*-toluenethiol: NMR ($CDCl_3$) δ 2.3 (s, H), 3.4 (s, 1H), 7.1 (m, 4H); NMR of mixture ($CDCl_3$) δ 0.03 (s), 2.3 (s), 3.4 (s), 7.1 (m). The NMR spectrum of the mixture is consistent with the mass spectral findings. Attempts to isolate *p*-toluenethiol (*m/e* 124) by GC on 6 ft. × 1/4 in. 15% SE 30 on Chromosorb W column resulted in the formation of *p,p'*-dimethyldiphenylsulfide: NMR ($CDCl_3$) δ 2.34 (s, 3H), 7.1 (m, 4H); IR (CCl_4 soln.) 3080, 3040, 2960, 1495, 1250, 850 cm^{-1}; mass spectrum (70 eV) *m/e* (rel. intensity) 214 (100), 199 (5), 122 (8), 91 (40); Exact mass calculated for $C_{14}H_{14}S$, *m/e* 214.0816; found: *m/e* 214.0809 ± 0.0011.

Flash vacuum pyrolysis of the sodium salt of tosylhydrazine

The sodium salt of tosylhydrazine, prepared by treatment of one equivalent of tosylhydrazine with one equivalent of sodium methoxide in methanol, was pyrolyzed under the same conditions as above. Analysis, by NMR, of the condensed material shows only *p*-toluenethiol, as identified by comparison of NMR to an authentic sample. NMR ($CDCl_3$) δ 2.3 (s, 3H), 3.4 (s, 1H), 7.1 (m, 4H).

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