THE PREPARATION AND PROPERTIES OF CYCLIC SILICON OLEFINS AND DIENE SYSTEMS

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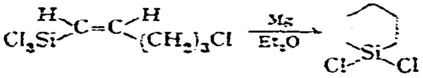
It was previously reported[1,2] from our Laboratory, that a convenient entry into the 1-sila-2-cyclopentene ring system is afforded via a Grignard cyclization of the appropriate open-chain organochlorosilane. We now wish to report an extension of this method to the preparation of 1,1-dichloro-1-sila-2-cyclohexene (I). We were able, moreover, to convert the latter compound to the unique cyclic silicon diene system, 1,1-dichloro-1-sila-2,4-cyclohexadiene (III).

In keeping with our earlier findings[3] on the mode of addition of trichlorosilane to terminal acetylenes in the presence of organic peroxides, treatment of 5-chloro-1-pentyne with trichlorosilane in the presence of benzoyl peroxide as initiator resulted predominantly in *trans* addition, affording the *cis* olefin as the major product (eqn. 1). The *cis*- to *trans*-olefin ratio was on the order of 3:1. The two isomeric olefins were separated by vapor phase chromatography, and structural assignments were made on the basis of infrared and NMR spectra of the products.

$$Cl_3SiH + HC{\equiv}C(CH_2)_3Cl \xrightarrow{\text{peroxide}} \underset{cis/trans\,=3}{Cl_3SiCH{=}CH(CH_2)_3Cl} \qquad (1)$$

Ring closure to form 1,1-dichloro-1-sila-2-cyclohexene (I) proceeded smoothly (eqn. 2) when the original olefin mixture contained either 75 or 85 % of *cis*-5-chloro-1-(trichlorosilyl)-1-pentene, although the yield of cyclic product was increased from 44 to 59 % in the latter instance.

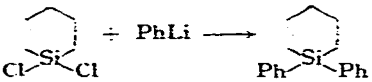


(I)

(2)

No attempt was made to study possible *cis–trans* isomerization under cyclization conditions, although it has been shown[1] that the next lower member of the series, *trans*-4-chloro-1-(trichlorosilyl)-1-butene, undergoes isomerization under similar conditions.

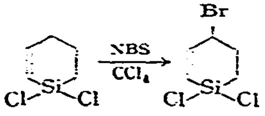
In the way of further confirmation of structure (I), its diphenylated derivative, 1,1-diphenyl-1-sila-2-cyclohexene, was prepared and characterized (eqn. 3).



(I)

(3)

The availability of appreciable quantities of (I) via the described route prompted speculation as to the possibility of introducing a conjugated diene moiety into the six-membered ring system. The approach undertaken consisted of allylic bromination of (I), followed by subsequent dehydrohalogenation. Bromination was readily accomplished with N-bromosuccinimide (eqn. 4), yielding, as the principal product, a compound to which we have assigned the structure 1,1-dichloro-4-bromo-1-sila-2-cyclohexene (II) based upon its infrared and NMR spectra.

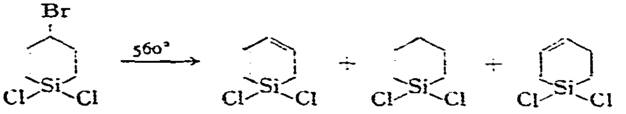


(I) (II)

(4)

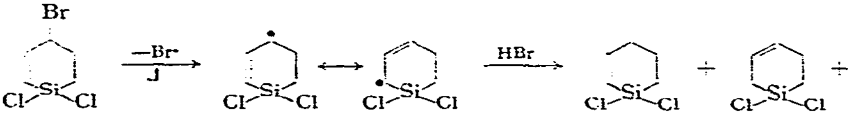
The bromination step, however, undoubtedly produced other brominated species, as evidenced by the boiling point range exhibited by the reaction product. It would appear reasonable that 1,1-dichloro-2-bromo-1-sila-3-cyclohexene could arise via bromine introduction at the 2-position of the allylic radical system, while formation of dibrominated products can also be envisioned. Unfortunately, it was not possible to ascertain the identity of the minor components of the brominated mixture, since attempted separation of the allylic bromides by VPC invariably led to decomposition of the sample.

Although dehydrohalogenation of chloro-substituted cyclic silicon systems had previously been carried out successfully in our Laboratory by the use of quinoline and ferric chloride[2], treatment of the brominated mixture obtained above (eqn. 4) with these reagents led only to partial or total destruction of starting material. Pyrolysis at 560°, however, afforded as the principle product 1,1-dichloro-1-sila-2,4-cyclohexadiene (III), along with minor amounts of 1,1-dichloro-1-sila-2-cyclohexene and 1,1-dichloro-1-sila-3-cyclohexene (IV).



(II) (III)(78%) (I)(11%) (IV)(11%)

Spectral data obtained on (III) were quite consistent with the proposed structure: its infrared spectrum showed two sharp bands of equal intensity in the olefinic region, at 6.11 μ and 6.45 μ, while the UV spectrum of this compound gave a $\lambda_{max} = 265$ mμ. Although conclusive evidence was lacking, the production of (I) and (IV) during pyrolysis can be rationalized by a scheme similar to that depicted in eqn. (5).



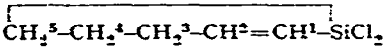
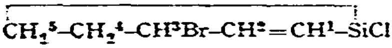
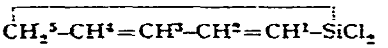
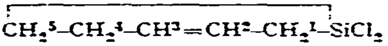
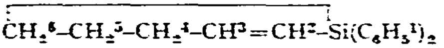
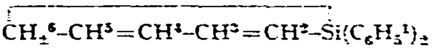
(II) (I) (IV)

(5)

Additional evidence as to the identity of (III) was obtained by phenylation of the mixture arising from pyrolysis, followed by reaction with maleic anhydride. The

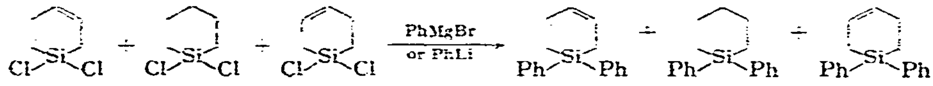
TABLE 1

NMR SPECTRA OF VARIOUS SILANES[a,b,c]

Silane	*τ-Values*
(1) *cis*-$Cl–CH_2^5–CH_2^4–CH_2^3–CH^2=CH^1–SiCl_3$	4.21 (H^1 doublet), 3.32 (H^2 pair of merged triplets), 7.39 (H^3 quartet), 8.00 (H^4 quartet), 6.47 (H^5 triplet)
(2) *trans*-$Cl–CH_2^5–CH_2^4–CH_2^3–CH^2=CH^1–SiCl_3$	4.15 (H^1 two triplets), 3.30 (H^2 two triplets), 7.52 (H^3 quartet), 7.99 (H^4 quartet), 6.49 (H^5 triplet)
(3)  $CH_2^5–CH_2^4–CH_2^3–CH^2=CH^1–SiCl_2$	4.13 (H^1 two triplets), 3.09 (H^2 two triplets), 7.48–8.23 (H^3, H^4 complex pattern), 8.69 (H^5 multiplet
(4)  $CH_2^5–CH_2^4–CH^3Br–CH^2=CH^1–SiCl_2$	3.04 (H^2 two doublets), 4.10 (H^1 doublet), 5.20 (H^3 quartet), 7.52 (H^4 multiplet), 8.00–8.80 (H^5 complex pattern)
(5)  $CH_2^5–CH^4=CH^3–CH^2=CH^1–SiCl_2$	3.06 (H^2 two quartets), 3.91 (H^1, H^3, H^4 multiplet), 7.82 (H^5 doublet)
(6)  $CH_2^5–CH_2^4–CH^3=CH^2–CH_2^1–SiCl_2$	4.28 (H^2, H^3 multiplet), 7.54 (H^4 multiplet), 8.15 (H^1 multiplet), 8.73 (H^5 triplet)
(7)  $CH_2^6–CH_2^5–CH_2^4–CH^3=CH^2–Si(C_6H_5^1)_2$	2.73 (H^1 multiplet), 3.26 (H^3 one triplet of a pair), 4.08 (H^2 doublet), 7.61–8.28 (H^4, H^5 complex pattern), 8.87 (H^6 multiplet)
(8)  $CH_2^6–CH^5=CH^4–CH^3=CH^2–Si(C_6H_5^1)_2$	2.73 (H^1 multiplet), 3.21 (H^3 two quartets), 4.01 (H^2, H^4, H^5 multiplet), 8.08 (H^6 doublet)

[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. A Varian A-60 NMR spectrometer was employed. Chemical shifts are measured to the estimated center of a singlet or multiplet. [b] In the case of each of the spectra listed, the peak areas are quite consistent with the proton assignments made. [c] The values listed for entry (6) in this table are taken from the Ph.D. thesis of J. L. Noe, Purdue University, 1964. The compound was prepared by subjecting a mixture of ring-chlorinated 1,1-dichloro-1-silacyclohexanes to dehydrohalogenation. (Found: C, 36.21; H, 5.16; Cl, 42.10. $C_5H_8SiCl_2$ calcd.: C, 35.93; H, 4.82; Cl, 42.44%.)

reaction of (III) with excess phenylmagnesium bromide or phenyllithium, however, afforded only poor yields of 1,1-diphenyl-1-sila-2,4-cyclohexadiene (eqn. 6). Analysis by vapor phase chromatography showed that the phenylated species (V), (VI) and (VII) were produced in almost equal amounts from this reaction*.



(III)(78%) (I)(11%) (IV)(11%) (V)(30%) (VI)(35%) (VII)(35%) (6)

Either the mixture thus produced, or (V) alone (after VPC separation) was found to give the same Diels–Alder adduct when treated with maleic anhydride, thus confirming the presence of a conjugated diene system.

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* Analytical conditions (VPC) could not be found for the separation of (VI) from (VII), but the infrared spectrum of a mixture of these two compounds collected by VPC, strongly indicated that the mixture consisted of these two monoolefins.

TABLE 2

INFRARED SPECTRA OF VARIOUS SILANES[a,b,c]

Silane	*Infrared absorptions* (μ)
(1) *cis*-5-Chloro-1-(trichlorosilyl)-1-pentene	3.4, 6.2, 6.9, 7.3, 7.6, 13.4, 14.2
(2) *trans*-5-Chloro-1-(trichlorosilyl)-1-pentene	3.4, 6.1, 6.9, 7.6, 10.1, 12.2, 13.4
(3) 1,1-Dichloro-1-sila-2-cyclohexene	3.44, 6.27, 6.87, 7.01, 7.14, 7.34, 7.49, 7.85, 8.08, 8.45, 8.92, 8.98, 10.36, 11.19, 12.64, 12.90, 14.3, 15.1
(4) 1,1-Dichloro-4-bromo-1-sila-2-cyclohexene	3.40, 6.28, 6.93, 7.14, 7.31, 7.42, 7.82, 8.38, 8.51, 8.74, 9.10, 9.29, 10.45, 10.75, 11.66, 11.82, 12.20, 12.37, 12.68, 13.3, 14.3
(5) 1,1-Dichloro-1-sila-2,4-cyclohexadiene	3.27, 6.11, 6.45, 7.24, 7.35, 7.92, 8.45, 8.93, 11.55, 12.20, 14.4
(6) 1,1-Dichloro-1-sila-3-cyclohexene	3.34, 3.47, 6.08, 6.93, 7.20, 7.90, 8.31, 8.8, 9.6, 10.8, 11.6, 12.1, 12.8
(7) 1,1-Diphenyl-1-sila-2-cyclohexene	3.26, 3.35, 3.42, 6.27, 6.72, 6.87, 6.98, 7.11, 7.50, 8.44, 9.01, 10.02, 10.35, 11.21, 12.85, 13.1, 13.75, 14.3, 15.1
(8) 1,1-Diphenyl-1-sila-2,4-cyclohexadiene	3.22, 6.16, 6.48, 6.74, 7.00, 7.26, 7.42, 9.02, 11.69, 12.6, 13.20, 13.8, 14.15, 14.4

[a] All spectra were obtained on neat samples. [b] All spectra except for compounds (1), (2) and (6) were obtained on a Perkin Elmer Model 221 spectrophotometer. The spectra of (1), (2) and (6) were obtained on a Perkin Elmer Infracord, Model 137. [c] The values listed for compound (6) were taken from the Ph.D. thesis of J. L. Noe, Purdue University, 1964.

In Tables 1 and 2 are listed the NMR and infrared spectra of the various silanes, both cyclic and open-chain, which have been synthesized and reported in this paper.

EXPERIMENTAL

5-Chloro-1-(trichlorosilyl)-1-pentene

Hydrosilation of 5-chloro-1-pentyne was carried out in a flask equipped with a Friedrichs condenser and mercury trap (closed system). There was mixed 70 g (0.683 mole) of the acetylenic chloride,* 14 g (0.0578 mole) of benzoyl peroxide, 201 g (1.48 mole) of trichlorosilane and 600 ml cyclohexane, and the mixture brought to reflux. After a reaction time of 70 h solvent and excess reagents were removed under aspirator vacuum and the residue distilled in a Todd apparatus. There was obtained 88.1 g (54%) of 5-chloro-1-(trichlorosilyl)-1-pentene (*cis* + *trans*), boiling at 55–66°/*ca.* 1 mm. Analysis of the reaction mixture by vapor phase chromatography before distillation (Perkin Elmer Model 154, 10′ QF-1 column, 150°) indicated the *cis* isomer comprised 74% of the product.

The addition was also carried out on a larger scale. In another run, a mixture of 1800 ml cyclohexane, 42 g (0.173 mole) of benzoyl peroxide, 200 g (1.95 mole) of the acetylenic chloride and 536 g (3.96 mole) of trichlorosilane yielded, after workup, 264 g (51%) of the adduct. (Found: C, 25.68; H, 3.45; Cl, 59.23. $C_5H_8SiCl_4$ calcd.: C, 25.23; H, 3.39; Cl, 59.60%.)

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* Purchased from Farchan Research Laboratories, Wickliffe, Ohio.

1,1-Dichloro-1-sila-2-cyclohexene

In a 5-liter three-neck flask fitted with condenser, stirrer and nitrogen line were placed 2500 ml of anhydrous ethyl ether, 120 g (4.93 g-atom) of powdered magnesium and *ca.* 1 ml of methyl iodide. Reflux was initiated and 123.1 g (0.517 mole) of 5-chloro-1-(trichlorosilyl)-1-pentene (about 85% *cis*) in five times its volume of anhydrous ethyl ether was added dropwise. After stirring for 18 h, salts were filtered off, and the ether was removed under aspirator vacuum. A final filtration was followed by distillation, yielding 51 g (59%) of 1,1-dichloro-1-sila-2-cyclohexene boiling at 59–61°/15 mm. Analysis by vapor phase chromatography (Perkin Elmer Model 154, 12′ QF-1 column, 154°) indicated this material was at least 95% pure. The large dilution factor employed in the reaction is necessitated by the large quantity of flocculant salts which are produced. When magnesium shavings were used in place of the powdered metal, the cyclization was incomplete and some starting material was recovered. (Found: C, 36.30; H, 4.67; Cl, 43.06. $C_5H_8SiCl_2$ calcd.: C, 35.94; H, 4.82; Cl, 42.44%.)

In another run, employing 322 g (1.35 mole) of 5-chloro-1-(trichlorosilyl)-1-pentene (*ca.* 75% *cis*-isomer) and 125 g (5.15 g-atom) of powdered magnesium there was obtained, after workup similar to that above, 100.1 g (44%) of cyclic product.

Bromination of 1,1-dichloro-1-sila-2-cyclohexene

In a one-neck flask equipped with condenser and mercury trap were placed 600 ml of carbon tetrachloride, 86.7 g (0.519 mole) of 1,1-dichloro-1-sila-2-cyclohexene and 92.7 g (0.521 mole) of N-bromosuccinimide. The mixture was held at reflux for 5 h, and filtration was followed by removal of solvent under aspirator vacuum. Distillation afforded the following fractions (3.1 mm): Forerun to 74°, 0.4 g; 74°–81.5°, 69.9 g; 81.5–88°, 29.3 g; 88–115°, 9.9 g. While infrared spectra of the first and last fractions indicated some degree of contamination, all fractions appeared to be mostly 1,1-dichloro-4-bromo-1-sila-2-cyclohexene, although the presence of more highly brominated products was suspected. All attempts to analyze samples of the allylic bromide by vapor phase chromatography led to decomposition. A redistilled sample (b.p. 64–8° at 1.5 mm) analyzed correctly and gave an NMR and infrared spectrum consistent with the allylic structure. (Found: C, 24.87; H, 2.97; Br, 32.36; Cl, 28.73. $C_5H_7SiBrCl_2$ calcd.: C, 24.41; H, 2.87; Br, 32.49; Cl, 28.83%.)

1,1-Dichloro-1-sila-2,4-cyclohexadiene

1,1-Dichloro-4-bromo-1-sila-2-cyclohexene (111.8 g, containing some more highly brominated material) was passed through a tube filled to a height of 10″ with 6 cm glass beads at 560° under nitrogen flow. Distillation of the pyrolysate yielded 26.4 g of material boiling at 54–60°/7.8 mm. The pot residue from this distillation was taken up in petroleum ether (35–7°) and repyrolyzed, affording an additional 3.9 g of the diene. Analysis by vapor phase chromatography of the combined distillates (F and M Model 500, 5′ FFAP column, 80°) indicated the presence of three compounds in the ratio of 6:6:41. Collection of the first peak (conditions as above, but at 75°) followed by comparison of its infrared spectrum with that of an authentic sample showed it to be 1,1-dichloro-1-sila-3-cyclohexene, while the impurity represented by the second small peak was identified as 1,1-dichloro-1-sila-2-cyclohexene by comparison of its retention time with that of an authentic sample. The third peak, after collection, was shown by its NMR and IR spectra (see Tables 1 and 2) to be the desired diene. (Found: C, 36.56; H, 3.88; Cl, 42.61. $C_5H_6SiCl_2$ calcd.: C, 36.38; H, 3.67; Cl, 42.96%.)

Unsuccessful attempts at dehydrobromination of 1,1-dichloro-4-bromo-1-sila-2-cyclohexene

A. With ferric chloride. Approximately 1 ml of the bromo compound was heated at 140° with a trace of anhydrous $FeCl_3$ in a closed system for 24 h. Distillation at the end of this time afforded only a small amount of starting material as the only volatile product, identified by boiling point (72.4°/2.7 mm) and infrared comparison.

In another run, 5.0 g of the bromide and a trace of $FeCl_3$ were heated to 200° in a pot attached to a small distillation set-up. After 30 h, only a few drops of material had distilled over; an infrared spectrum taken on this sample indicated little olefin adsorption. Distillation of the pot residue under reduced pressure yielded only about 0.3 ml of liquid, b.p. 28–30°/0.34 mm (ambient, 27°) which VPC indicated was a mixture with at least five major components. No starting material was recovered.

B. With quinoline. 1,1-Dichloro-4-bromo-1-sila-2-cyclohexene, 5.0 g, was added to 25 ml of quinoline and heated at 230–5° for 2.5 h in a small distillation assembly. No liquid distilled, and upon cooling, the material in the pot solidified to a brown glassy substance which yielded no volatiles upon attempted distillation under reduced pressure.

1,1-Diphenyl-1-sila-2-cyclohexene

1,1-Dichloro-1-sila-2-cyclohexene (4.0 g, 0.0239 mole) was diluted with about three times its volume of anhydrous ethyl ether and added to a three-fold molar excess of phenyllithium. After the addition was completed, the mixture was allowed to stir for several hours and then was worked up in the usual manner. Distillation (after a forerun of biphenyl) gave 4.1 g (70%) of product boiling at 140–8° at 0.11 mm. A sample collected by VPC (Aerograph Autoprep, 15′ Carbowax 20 M T.P.A. prep. column, 220°) was submitted for elemental analyses (n_D^{27} 1.5934). See Tables 1 and 2 for the NMR and infrared spectra of this compound. (Found: C, 81.69; H, 7.28. $C_{17}H_{18}Si$ calcd.: C, 81.60; H, 7.20%.)

1,1-Diphenyl-1-sila-2,4-cyclohexadiene

To a stirred solution of a two-fold excess of phenyllithium in anhydrous ethyl ether was slowly added 29.0 g (0.176 mole) of 1,1-dichloro-1-sila-2,4-cyclohexadiene dissolved in an equal volume of anhydrous diethyl ether. After addition had been completed, stirring was continued for 40 min longer, and the mixture hydrolyzed. The organic layer was separated, dried, solvent removed, and the residue distilled at 0.4 mm. After a forerun of *ca.* 1 ml of biphenyl (70–72°), 4.2 g of material was collected, b.p. 128–142°. Analysis by vapor phase chromatography (F and M Model 720, 12′ DEGS column, 195°) disclosed that this cut contained three compounds in the ratio 35:35:30. Separation of the last from the first two peaks was effected on a 15′ prep. Carbowax 20 M T.P.A. column (Autoprep, 220°). It was found that the last peak was 1,1-diphenyl-1-sila-2,4-cyclohexadiene (see Tables 1 and 2 for NMR and infrared spectra), n_D^{27} 1.6090, while the IR and NMR spectra of the first two peaks (collected together – incomplete separation) indicated a mixture of 1,1-diphenyl-1-sila-2-cyclohexene and 1,1-diphenyl-1-sila-3-cyclohexene. (Found: C, 82.03, H, 6.26. $C_{17}H_{16}Si$ calcd.: C, 82.21; H, 6.49%.)

Reaction of maleic anhydride with 1,1-diphenyl-1-sila-2,4-cyclohexadiene

Maleic anhydride (0.15 g) and a 0.40 g sample of 1,1-diphenyl-1-sila-2,4-cyclohexadiene containing some biphenyl and 2- and 3-cyclic olefins as contaminants were dissolved in octane and heated at reflux for 4 h. The mixture became cloudy, but evaporation of the solvent under reduced pressure afforded only a thick liquid. Upon standing in the cold for a period of weeks however, this oil partially solidified. It was recrystallized from benzene to give a white solid, which, upon sublimation, (170°/0.2 mm) yielded a white powder which was analytically pure and had a melting point of 194–5° (uncorrected, Nalge melting point block).

In another instance, 0.0165 g of the diene (VPC collected) and 0.0140 g of maleic anhydride were mixed neat and heated at 120° for 0.5 h. At the end of this time only solid remained in the reaction tube, excess anhydride having sublimed to the sides of the vessel. The adduct was recrystallized from benzene to yield 0.0036 g of white powder which melted at 188–92°. (Found: C, 72.55; H, 5.52. $C_{21}H_{18}SiO_3$ calcd.: C, 72.81; H, 5.24%.)

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SUMMARY

A synthesis of 1,1-dichloro-1-sila-2-cyclohexene has been achieved. This olefin has been phenylated by means of phenyllithium and 1,1-diphenyl-1-sila-2-cyclohexene thus prepared. Bromination of 1,1-dichloro-1-sila-2-cyclohexene with N-bromosuccinimide produced several products, one of which was identified as 1,1-dichloro-4-bromo-1-sila-2-cyclohexene. Pyrolysis of the latter produced principally 1,1-dichloro-1-sila-2,4-cyclohexadiene. This cyclic diene reacted with phenyllithium to produce 1,1-diphenyl-1-sila-2,4-cyclohexadiene, a compound which reacted further with maleic anhydride to form a Diels–Alder adduct.

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