1,1-Diphenylsila-2-cyclohexanone[1]

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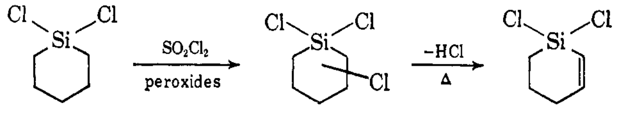
Received February 19, 1965

1,1-Diphenylsila-2-cyclohexene has been synthesized from 1-trichlorosilyl-5-chloro-1-pentene. Hydroboration of this alkene and of vinyltriphenylsilane gives predominantly the product where boron is attached to the carbon adjacent to silicon. While oxidation of 1,1-diphenylsila-2-cyclohexanol with chromium trioxide gives mainly cleavage products, oxidation with dicyclohexylcarbodiimide in dimethyl sulfoxide gave 1,1-diphenylsila-2-cyclohexanone, the first reported cyclic α-silyl ketone, in good yield. The spectral properties of this compound appear normal for a phenylsilylalkyl ketone, suggesting no significant ring strain is present. An explanation for the predominating silicon–carbon bond cleavage observed when chromium trioxide is used as oxidant is proposed.

The unusual spectral properties[2,3] and chemical behavior[4] of α-silyl ketones such as benzoyltriphenylsilane suggested that cyclic α-silyl ketones should also possess interesting properties, and hence the synthesis of a 2-silacyclohexanone was undertaken. Only two related compounds have been reported previously. Benkeser and Bennett[5] reported the synthesis of 1,1-dimethylsila-4-cyclohexanone and suggested, by comparison with the analogous cyclohexanone, that the lower carbonyl stretching frequency and the larger dissociation constant of the cyanohydrin found for the silicon compound was due to ring strain caused by introduction of the larger silicon atom in the ring. Wittenberg, Talukdar, and Gilman[6] have reported the synthesis of the 2,3-benzo derivative of this compound, namely, 2,3-benzo-1,1-diphenyl-1-silacyclohexen-2-one-4. The carbonyl stretching frequency in this compound was identical with that of 1-tetralone, suggesting no particular effects attributable to silicon in the ring or, as Gilman expressed it, the influence of the increased ring size was compensated by the influence of the diphenylsilyl group in an *ortho* position to the carbonyl group.

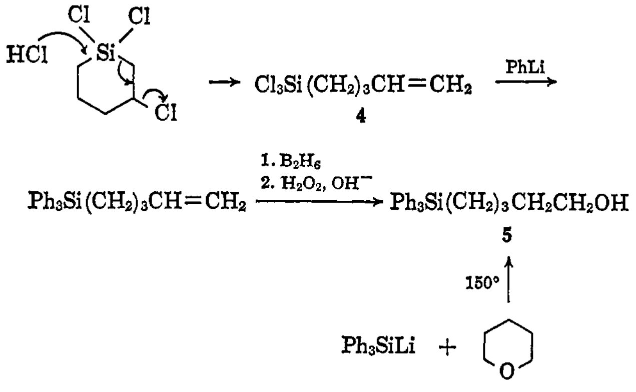
The carbonyl group in the above compounds was introduced in a conventional manner, *i.e.*, ring closure by pyrolysis of the thorium salt of a dicarboxylic acid or by Friedel–Crafts cyclization where, in each case, the reacting groups were sufficiently remote from silicon for abnormal reactions to be largely avoided. In the current synthesis, neither these methods nor the methods previously employed, *i.e.*, conversion of reactive benzylic hydrogens to dibromides which could be hydrolyzed[2] or oxidation of a hydroxy group created adjacent to silicon by reaction of a silylmetallic with an aldehyde,[7] appeared particularly promising as methods for creating a carbonyl group next to silicon in a ring.

It was decided to attempt introduction of a hydroxyl group next to silicon by hydroboration of a 1-silylcyclohex-2-ene (3) and then to oxidize the hydroxyl group to a carbonyl function. Two general approaches to a silacyclohex-2-ene were investigated. 1,1-Dichlorosilacyclohexane (1) is readily prepared[8] and free-radical chlorination followed by dehydrohalogenation would lead to the desired product 3 among others.



1 2 3

Monochlorination of 1,1-dichlorosilacyclohexane readily occurred giving a mixture of 1,1-dichlorosilachlorocyclohexanes as found by Benkeser[9] for the corresponding silacyclopentane system. However, attempted dehydrohalogenation with refluxing quinoline gave mainly tars and little volatile material. Pyrolysis of the halide at 400° to effect dehydrohalogenation gave as the major product 5-trichlorosilyl-1-pentene (4), as shown by its subsequent phenylation and oxidation *via* the borane to 5-triphenylsilyl-1-pentanol (5) which was independently synthesized by cleavage of tetrahydropyran with triphenylsilyllithium after the method of Gilman.[10] The formation of 5-trichlorosilyl-1-pentene may be explained by a β elimination of the β-chloroalkylsilane expected to predominate in the system,[9] possibly facilitated by attack of hydrogen chloride, or by a second molecule of chloroalkylsilane on silicon.



The second approach attempted, also used by Benkeser,[9] was synthesis and cyclization of a 1-chlorosilyl-5-chloro-1-pentene (6) in which the required double bond was established prior to creation of the ring. The reactions employed are outlined below. Trichlorosilane was added to 5-chloro-1-pentyne in the presence

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[1] From the M.A. Thesis of J. B. Pierce, University of Toronto, 1963. Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1964; Abstracts, p. 12P.

[2] A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, **82**, 5102 (1960).

[3] A. G. Brook, R. Kivisikk, and G. E. LeGrow, *Can. J. Chem.*, **43**, 1175, (1965).

[4] A. G. Brook and N. V. Schwartz, *J. Org. Chem.*, **27**, 2311 (1962).

[5] R. A. Benkeser and E. W. Bennett, *J. Am. Chem. Soc.*, **80**, 5414 (1958).

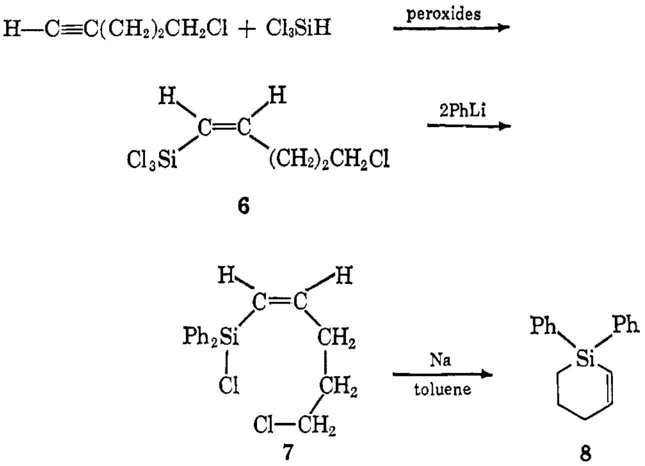
[6] D. Wittenberg, P. B. Talukdar, and H. Gilman, *ibid.*, **82**, 3608 (1960).

[7] G. E. LeGrow, M.A. Thesis, University of Toronto, 1962.

[8] (a) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954); (b) A. Bygden, *Ber.*, **48**, 1236 (1915).

[9] R. A. Benkeser, *et al.*, *J. Am. Chem. Soc.*, **86**, 2446 (1964).

[10] H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 2680 (1958).



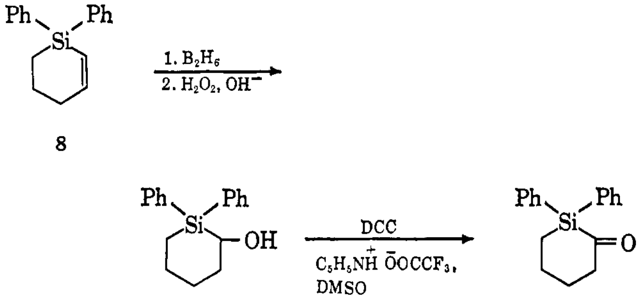
6 7 8

of peroxide, conditions known to favor *trans* addition and hence the formation of the desired *cis* alkene.[11] The resulting 1-trichlorosilyl-5-chloro-1-pentene (**6**) appeared to be a mixture of *cis* and *trans* isomers, based on gas chromatography of its trimethylsilyl derivative. Since the isomers could not be easily separated, the mixed trichlorosilanes were converted to diphenylchlorosilyl derivatives with phenyllithium, and the *cis–trans* mixture of 1-diphenylchlorosilyl-5-chloro-1-pentenes (**7**) was cyclized using sodium in refluxing toluene to give 1,1-diphenylsila-2-cyclohexene (**8**) in about 50% yield.

Diphenylsilacyclohexene, a colorless oil, shows carbon–carbon double-bond stretching absorption at 6.29 μ close to the value of 6.25 μ found for dichlorosilacyclopentene.[9] The n.m.r. spectrum is complex. In the neat liquid two complex aromatic bands centered at about δ = 7.55 and 7.16 p.p.m. are ascribable to the four *ortho* and six *meta* plus *para* hydrogens, these bands coalescing in dilute solution to a single complex band, a phenomenon previously observed by Cawley and Danyluk,[12] and explained by them in terms of ring-current effects. One vinyl proton appeared as a multiplet, partly obscured by the aromatic band, at about δ = 6.9 p.p.m. and the other vinyl proton (adjacent to silicon) as two broad bands separated by about 15 c.p.s. at about δ = 5.85 and 6.09 p.p.m. This part of the spectrum was very similar to that reported by Seyferth[13] for *cis*-propenyltrimethylsilane. The methylene region was exceedingly complex, strong multiplets (and their tentative assignments) centered at about δ = 2.0 (CH_2CH=), 1.21 ($CH_2CH_2CH_2$), and 1.0 p.p.m. (CH_2Si) being observed. The integrated areas were in reasonable agreement with these assignments.

Diphenylsilacyclohexene was hydroborated and treated with alkaline hydrogen peroxide following the general conditions of Brown.[14] This method of introducing a hydroxyl group adjacent to silicon appeared promising since Seyferth[15] had noted that trimethylvinylsilane gave substantially more addition of boron on the carbon adjacent to silicon (37%) than occurred on the internal carbon of its analog *t*-butylethylene (6%). It was found that vinyltriphenylsilane similarly gave substantial α addition, the mixture of carbinols formed on treatment with alkaline hydrogen peroxide being about 80% 1-triphenylsilylethanol and 20% 2-triphenylsilylethanol. Hydroboration and oxidation of diphenylsilacyclohexene (**8**) appeared to give exclusively the α-carbinol 1,1-diphenylsila-2-cyclohexanol (**9**). The infrared spectrum of the distilled product showed infrared OH absorption only at 2.78 μ, characteristic of α-silylcarbinols, and no absorption at 2.76 μ, characteristic of β-silylcarbinols (*e.g.*, the triphenylsilylethanols). The n.m.r. spectrum showed the expected aromatic multiplet at δ = 7.4 p.p.m., a triplet centered at δ = 3.7 p.p.m. attributable to the hydrogen attached to the carbinol carbon, and a sharp singlet whose position at about δ = 2.4 p.p.m. was solvent and concentration sensitive (O–H) together with methylene bands in the 1.2–1.6-p.p.m. region. No additional weak bands were observed. Hence it appears that, if any β-carbinol were formed, either its amount is so small as to preclude detection by infrared or n.m.r. spectroscopy, or else it was destroyed during the work-up or distillation.

Conversion of diphenylsilacyclohexanol to 1,1-diphenylsila-2-cyclohexanone (**10**) was attempted using chromium trioxide–sulfuric acid in acetone and also was accomplished using a method recently described[16] employing dicyclohexylcarbodiimide (DCC) with pyridinium trifluoroacetate in dimethyl sulfoxide (DMSO). This latter method has been found to be exceedingly useful for the oxidation of α-silylcarbinols to α-silyl ketones.[17] Using this method, the oxidation occurred essentially quantitatively, no unchanged carbinol being detected in the infrared spectrum of the crude reaction product, and the desired ketone **10** was obtained as a very pale yellow crystalline solid, melting at 63–65°, in about 70% yield. The infrared spectrum showed a carbonyl stretching band at 6.07 μ, a position characteristic of an alkyl-α-silyl ketone, both acetyl-[2] and propionyltriphenylsilane[1] having been observed to absorb at 6.08 μ. The ultraviolet spectrum, as shown in Table I, is also similar to that observed previously for alkylsilyl ketones. The very pale yellow color of the compound is undoubtedly due to end absorption from the broad n–π^* multiplet extending into the visible region. The ketone was further characterized by its reduction back to 1,1-diphenylsila-2-cyclohexanol and by its reaction with methyl Grignard reagent to give 1,1-diphenylsila-2-methyl-2-cyclohexanol.



8 9 10

Use of chromium trioxide–sulfuric acid in acetone, a reagent which had been used with moderate success in some previous oxidations of alkylsilylcarbinols to

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[11] R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. O. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).

[12] S. Cawley and S. S. Danyluk, *J. Chem. Phys.*, **38**, 285 (1963).

[13] D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **1**, 138 (1963).

[14] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

[15] D. Seyferth, *ibid.*, **81**, 1844 (1959).

[16] K. E. Pfitzner and J. G. Moffatt, *ibid.*, **85**, 3027 (1963).

[17] Unpublished studies from these laboratories to be reported shortly.

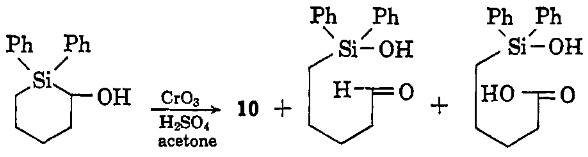
TABLE I

ULTRAVIOLET ABSORPTION SPECTRA FOR PHENYLSILYLALKYL KETONES

Compd.	π–π* (phenyl) λ, mμ	π–π* (phenyl) ε	n–π* (C=O) λ, mμ	n–π* (C=O) ε
1,1-Diphenylsila-2-cyclohexanone	264[a]	1520	367 (s)	196
	266	1225	383	284
	273	834	396	265
Acetyltriphenylsilane[b]	260[c]	1513	360	324
	265	1493	372	366
	272	1058	384	239
Propionyltriphenylsilane[d]	260[c]	1580	355	233
	265	1485	370	302
	272	987	385	243

[a] In cyclohexane. [b] See ref. 2. [c] In ethanol. [d] See ref. 7.

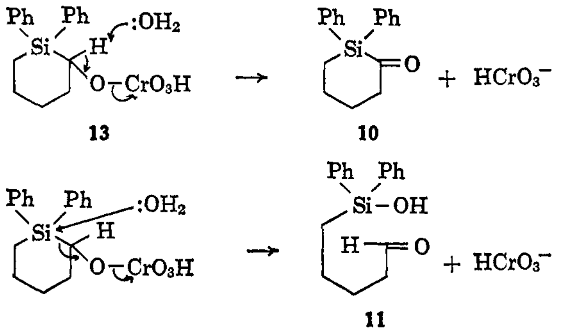
alkylsilyl ketones,[7] gave results highly inferior to those described above, but generally typical of α-silylcarbinol oxidations with this reagent, in that the major reaction occurring involved cleavage of the silicon carbinol–carbon bond. From 1,1-diphenylsilacyclohexanol were isolated the desired diphenylsilacyclohexanone (**10**, 5%), 5-diphenylhydroxysilyl-1-pentanol (**11**, 50%), and 5-diphenylhydroxysilylpentanoic acid (**12**, 7.5%). These were separated from each other and from recovered starting material by chromatography on silica gel. The aldehyde showed infrared absorption at 2.7 (SiO–H), 3.7 (aldehyde proton), and 5.78 μ (C=O). The n.m.r. spectrum showed the aldehyde proton at δ = 9.39 p.p.m. The acid, presumably derived from the aldehyde by further oxidation, showed infrared absorption at 2.7 (SiO–H), 3-4 (COOH, bonded), and 5.8 μ (C=O). The ketone could not be obtained pure from these reactions but showed the typical carbonyl absorption at 6.07 μ, and the same general infrared and ultraviolet spectra.



9 **11** **12**

Since the ketone **10** was stable toward hydrolysis by aqueous acid under the same acid conditions as those of the oxidation reaction, with no evidence for the formation of the hydroxysilylaldehyde, it is believed that the large amount of aldehyde **11** formed in the chromic acid oxidation is due not to cleavage of the ketone in the oxidizing medium, but rather to an alternative oxidation pathway.

Assuming the intermediacy of a chromate ester **13**, both normal oxidation and the bond-cleavage reaction can be written as a nucleophilic attack by water, either on the α-hydrogen of the chromate ester giving ketone, or on the α-silicon atom leading to the hydroxysilylaldehyde **11**, the susceptibility of silicon to nucleophilic attack being well known. While this mechanism cannot be confirmed at the present time, it explains satisfactorily the large amounts of silicon–carbon bond cleavage observed during this and other related[7] attempted oxidations with chromic acid.



13 **10** **11**

Since the spectroscopic properties of 1,1-diphenylsila-2-cyclohexanone, insofar as they have been investigated, appear completely normal for a phenylsilylalkyl ketone, it does not appear that replacement of carbon by a larger silicon atom in a six-membered ring has created any significant amount of ring strain. This conclusion has been made previously by West.[18] If this is true, the slightly longer carbonyl wave length observed by Benkeser for 1,1-dimethylsila-4-cyclohexanone (5.88 μ) relative to its carbon analog (5.85 μ)[4] could be attributed either to release of electrons through a field effect acting across the ring from silicon to the carbonyl group, or to inductive release of electrons by the dimethylsilyl group acting weakly through both pairs of intervening methylene groups to the carbonyl group. While it has been noted that noncyclic γ-ketosilanes show no bathochromic shift of the carbonyl stretching wave length relative to their carbon analogs,[19] an increase of the possible inductive release in the cyclic γ-ketosilane might produce the small effects observed. Inductive electron release by silicon has been attributed as the cause of the large bathochromic shifts observed in the carbonyl stretching wave length in α-silyl ketones, and the smaller shift observed in β-silyl ketones, relative to their carbon analogs.[19] Diphenylsilacyclohexanone is somewhat unstable in the presence of air, especially in solution, giving rise to a complex mixture of reaction products. Further studies of this reaction and of other cyclic α-silyl ketones are actively in progress.

Experimental

Reactions involving organometallics were run in an oxygen-free nitrogen atmosphere. Infrared spectra were determined on a Beckman IR8 instrument in carbon tetrachloride solution. Ultraviolet spectra were determined in cyclohexane on a Perkin-Elmer 350 instrument, and n.m.r. spectra, reported in p.p.m. (δ) from tetramethylsilane, were determined on a Varian A-60 instrument in carbon tetrachloride solution.

Dichlorosilachlorocyclohexane.—1,1-Dichlorosilacyclohexane was prepared from silicon tetrachloride and the di-Grignard reagent of 1,5-dibromopentane in 63% yield, b.p. 154–156°, n^{25}D 1.4667, as described by West.[8a] To 17 g. (0.101 mole) of refluxing dichlorosilacyclohexane was added over 3 hr. 14.4 g. (0.107 mole) of sulfuryl chloride and a small crystal of benzoyl peroxide every 15 min. during the course of the addition. The evolved gases were swept out of the system by a stream of nitrogen. After 4 hr. of additional reflux, distillation gave 6.5 g. (38%) of recovered starting material and 7.28 g. (35%) of dichlorosilachlorocyclohexane, b.p. 90–92° (24 mm.), n^{25}D 1.4931.

Anal. Calcd. for $C_5H_9Cl_3Si$: C, 29.5; H, 4.45. Found: C, 29.9; H, 4.34.

On one occasion, a second product, dichlorosiladichlorocyclohexane, was isolated in low yield from the residue, b.p. 120–124° (16 mm.), n^{25}D 1.5129.

Anal. Calcd. for $C_5H_8Cl_4Si$: C, 25.2; H, 3.57. Found: C, 25.2; H, 3.40.

Dehydrohalogenation of Dichlorosilachlorocyclohexane.—On attempted distillation of a mixture of 2.0 g. (0.0087 mole) of di-

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[18] R. West, *J. Am. Chem. Soc.*, **76**, 6015 (1954).

[19] A. G. Brook and J. B. Pierce, *Can. J. Chem.*, **42**, 298 (1964).

chlorosilachlorocyclohexane from 1.5 g. (0.0116 mole) of quinoline after brief reflux under nitrogen, during which time the mixture became red, a red tar formed and only a few drops of material distilled, b.p. 120–130°.

Vapor of 7.28 g. (0.0313 mole) of dichlorosilachlorocyclohexane was swept by a stream of nitrogen down a 2-ft.-long glass tube packed with glass helices and heated to 400° electrically. The reaction products were collected in a series of cold traps, the contents of which were combined. Distillation gave 2.45 g. (41%) of dehydrohalogenated product, b.p. 164–172°, $n^{25}\mathrm{D}$ 1.4657, infrared (C=C) 6.20 μ; 1.39 g. (19%) of recovered starting material, b.p. 97° (26 mm.), $n^{25}\mathrm{D}$ 1.4925; and considerable charred residue. The identity of the dehydrohalogenated product as 5-trichlorosilyl-1-pentene was established as follows.

5-Triphenylsilyl-1-pentene.—To 7.0 g. (0.0344 mole) of the above dehydrohalogenated material was added 0.120 mole of phenyllithium. After refluxing in ether–toluene at 90° for 18 hr. acid hydrolysis and work-up gave, either by distillation of the organic layer, b.p. 120–128° (0.03 mm.), or by chromatography on silica gel using as eluent 1:3 benzene–petroleum ether (b.p. 90–100°), a low-melting solid which after crystallization from pentane gave 2.0 g. (20%) of 5-triphenylsilyl-1-pentene, m.p. 45–45.5°, infrared (C=C) 6.10 μ.

Anal. Calcd. for $C_{23}H_{24}Si$: C, 84.2; H, 7.39. Found: C, 83.2; H, 7.18.

5-Triphenylsilyl-1-pentanol. A. By Hydroboration of 5-Triphenylsilyl-1-pentene.—To a mixture of 0.051 g. (0.0014 mole) of sodium borohydride and 0.5 g. (0.0020 mole) of 5-triphenylsilyl-1-pentene in 25 ml. of dry diglyme was added 0.059 g. (0.00044 mole) of anhydrous aluminum chloride in 25 ml. of diglyme. After heating the mixture at 40–50° for 3 hr. followed by careful hydrolysis using saturated ammonium chloride solution the organic layer was separated by ether extraction of the acidified aqueous layer. After removal of the ether, the residue, in tetrahydrofuran, was treated with 0.024 g. (0.0006 mole) of sodium hydroxide in 2 ml. of water and 0.25 ml. of 30% hydrogen peroxide. After stirring for 18 hr., work-up yielded an oil which was chromatographed on silica gel using benzene and chloroform as eluents. From the chloroform fractions a solid was isolated, which after recrystallization from hexane gave 0.20 g. (22%) of 5-triphenylsilyl-1-pentanol, m.p. 65–66°, shown by mixture melting point and infrared spectrum to be identical with the material prepared below.

Anal. Calcd. for $C_{23}H_{26}OSi$: C, 79.8; H, 7.53. Found: C, 78.9; H, 7.61.

B. By Cleavage of Tetrahydropyran.—To 1.25 g. (0.32 g.-atom) of lithium and 20 g. (0.040 mole) of hexaphenyldisilane was added slowly with stirring, 100 ml. of tetrahydropyran which had been distilled from lithium aluminum hydride. A dark brown color developed. The mixture was refluxed under nitrogen for 2 days and then 50 ml. of the dark brown solution was sealed in an ampoule under nitrogen and heated to 150° for 3 hr. Work-up essentially as described above, followed by rechromatography of the appropriate fraction, gave 0.21 g. of 5-triphenylsilyl-1-pentanol, m.p. 66–69°, identical with the material described above.

1-Trichlorosilyl-5-chloro-1-pentene.—5-Chloro-1-pentyne, b.p. 116–120°, $n^{25}\mathrm{D}$ 1.4448, was prepared from sodium acetylide and 1-chloro-3-bromopropane following the procedure of Campbell.[20] A mixture of 93 g. (0.61 mole) of 5-chloro-1-pentyne, 243 g. (1.80 moles) of trichlorosilane, and 14.5 g. (0.06 mole) of benzoyl peroxide in 1 l. of cyclohexane was stirred at 65° for 70 hr. Distillation at atmospheric pressure gave recovered trichlorosilane and cyclohexane and then, at reduced pressure, 111 g. (52%) of 1-trichlorosilyl-5-chloro-1-pentene, b.p. 125–130° (40 mm.), $n^{25}\mathrm{D}$ 1.4848, infrared (C=C) 6.23 μ.

Anal. Calcd. for $C_5H_8Cl_4Si$: Cl (titratable), 44.7. Found: Cl, 45.0.

1-Trimethylsilyl-5-chloro-1-pentene.—To 19 g. (0.080 mole) of 1-trichlorosilyl-5-chloro-1-pentene in dry ether was added 0.30 mole of methylmagnesium iodide at a rate to maintain gentle reflux. After stirring for 18 hr., the reaction mixture was hydrolyzed and worked up to give on distillation 8.1 g. (57%) of 1-trimethylsilyl-5-chloro-1-pentene, b.p. 89–90° (24 mm.), $n^{25}\mathrm{D}$ 1.4519, infrared (C=C) 6.23 μ.

Anal. Calcd. for $C_8H_{17}ClSi$: C, 54.5; H, 9.63. Found: C, 54.6; H, 9.66.

Gas chromatography on a 6-ft. isodecyl phthalate column at 135° showed partial resolution into two peaks of estimated areas 63:37, corresponding to the *cis* and *trans* isomers.

1-(Diphenylchlorosilyl)-5-chloro-1-pentene.—To 111 g. (0.465 mole) of 1-trichlorosilyl-5-chloro-1-pentene in 500 ml. of dry ether was added 0.93 mole of 3.96 *M* phenyllithium in ether. After 3 hr. a negative Color Test I was obtained and the ether was distilled and replaced by pentane. After filtration of the precipitated salts in a drybox, the filtrate and pentane washings were combined and distilled to give 112 g. (75%) of 1-diphenylchlorosilyl-5-chloro-1-pentene, b.p. 165–167° (0.2 mm.), $n^{25}\mathrm{D}$ 1.5744.

Anal. Calcd. for $C_{17}H_{18}Cl_2Si$: C, 63.4; H, 5.62. Found: C, 63.4; H, 5.65.

1,1-Diphenylsila-2-cyclohexene.—To a rapidly stirred refluxing mixture of 9.3 g. (0.40 g.-atom) of sodium in 500 ml. of dry toluene was added very slowly over 8 hr. 52 g. (0.162 mole) of 1-diphenylchlorosilyl-5-chloro-1-pentene in 500 ml. of dry toluene. The reaction mixture became deep blue. After an additional 8-hr. reflux, the mixture was carefully hydrolyzed and worked up to give 20.2 g. (50%) of diphenylsilacyclohexene, b.p. 132–135° (0.07 mm.), $n^{23}\mathrm{D}$ 1.5927, infrared (C=C) 6.29 μ.

Anal. Calcd. for $C_{17}H_{18}Si$: C, 81.6; H, 7.24. Found: C, 80.7; H, 7.23.

1,1-Diphenylsila-2-cyclohexanol.—To 5.0 g. (0.020 mole) of diphenylsilacyclohexene and 0.51 g. (0.0134 mole) of sodium borohydride in 30 ml. of dry diglyme was added 0.59 g. (0.0044 mole) of aluminum chloride in 20 ml. of diglyme. The resulting milky white suspension was stirred at room temperature for 18 hr. and then was carefully hydrolyzed with a saturated solution of ammonium chloride. After acidification the organic layer was ether extracted, and the ether layers were washed with water several times and then dried with anhydrous sodium sulfate. After removal of the ether under reduced pressure, the residue was dissolved in 50 ml. of tetrahydrofuran and 0.26 g. (0.0067 mole) of sodium hydroxide in 5 ml. of water was added, followed by 2.7 ml. (0.81 g., 0.0239 mole) of 30% hydrogen peroxide. The mixture became hot, and a curdy white precipitate formed. After stirring for 18 hr. ether and enough dilute hydrochloric acid to acidify the mixture were added. The ether layer and the ether washings were washed several times with water and then were dried. The ether was evaporated and distillation gave 3.6 g. (67%) of diphenylsilacyclohexanol, b.p. 160–164° (0.35 mm.), $n^{24}\mathrm{D}$ 1.5914.

Anal. Calcd. for $C_{17}H_{20}OSi$: C, 76.3; H, 7.54. Found: C, 75.8; H, 7.48.

1,1-Diphenylsila-2-cyclohexanone.—To a solution of 0.79 g. (0.00295 mole) of diphenylsilacyclohexanol in 5 ml. of dimethyl sulfoxide, dried over calcium hydride, was added 0.57 g. (0.00295 mole) of pyridinium trifluoroacetate. To this solution was added 0.91 g. (0.0044 mole) of dicyclohexylcarbodiimide, which dissolved. In a few seconds the solution became cloudy and warm, and then a white precipitate (dicyclohexylurea) formed, and the solution became pale yellow. The mixture was stirred magnetically for about 16 hr. under nitrogen, and then about 10 ml. of water and 15 ml. of hexane were added and vigorous stirring was continued for about 10 min. The contents of the flask was transferred to a separatory funnel using water and hexane, and, after shaking, the water layer was removed and the hexane layer was washed with water. The hexane layer was filtered through a bed of anhydrous sodium sulfate, as was a water-washed hexane extract of the original aqueous layer. Evaporation to dryness gave a solid residue, shown by infrared spectrum to be a mixture of diphenylsilacyclohexanone, 6.07 (SiC=O), 7.0, 9.0 μ (Si–Ph), and dicyclohexylurea, 2.90, 2.99 (N–H), 5.78, 5.89 μ (C=O), but no carbinol (2.78 μ, C–O–H) could be detected. Recrystallization from a minimum of methanol gave 0.40 g. (51%) of very pale yellow crystals, almost colorless as thin plates but pale yellow as larger chunks, m.p. 62–65°. An additional 0.15 g. (19%) was obtained by partial evaporation of the mother liquor followed by recrystallization. Recrystallization raised the melting point to 63–65°. The infrared spectra showed absorption at 6.07 (Si–CO–alkyl) and 7.0 and 9.0 μ (Si–Ph). An identical spectrum was obtained a week later from a sample maintained in the dark under nitrogen, but a carbon tetrachloride solution exposed to light and air showed considerable change over 1–2 days. The n.m.r. spectrum showed com-

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plex absorption at $\delta = 7.1–7.6$ (aromatic H), a distorted triplet centered at 2.35 ($-CH_2-CO$), a multiplet centered at 1.95 (CH_2-CH_2), and a distorted triplet centered at 1.58 p.p.m. ($Si-CH_2$); integration showed the peak areas to be in the ratio 10:2:4:2 as predicted.

Anal. Calcd. for $C_{17}H_{18}OSi$: C, 76.8; H, 6.73. Found: C, 76.8; H, 6.76.

Oxidation of Diphenylsilacyclohexanol.—To 4.77 g. (0.0178 mole) of diphenylsilacyclohexanol in 75 ml. of acetone, maintained at 0° in an ice bath was added slowly over 20 min. a solution of 1.17 g. (0.0117 mole) of chromium trioxide and 0.76 ml. (0.0137 mole) of 96% sulfuric acid in 5 ml. of water. The mixture was stirred for 5 min. after addition was complete and then was extracted with ether several times. After drying, and removal of the ether, the residue showed infrared absorption at 2.7 (SiO–H), 2.78 (weak, α-hydroxysilane), 3.7 (O=CH), 5.80, 5.85 (broad, C=O), and 6.08 μ (Si–CO–alkyl). The mixture was chromatographed on silica gel, using 1:1 hexane–benzene, benzene, 1:1 benzene–chloroform, and then chloroform as eluents; 25-ml. fractions were collected, and the progress of the chromatography was followed by infrared absorption spectrum in the 2.5–4- and 5.7–6.1-μ regions. The compounds obtained were as follows: (a) 1,1-diphenylsila-2-cyclohexanone (fractions 9–27, benzene), 0.25 g. (5%); (b) recovered diphenylsilylcarbinol (fractions 24–39, benzene), 0.3 g. (6%) (this material was not in general found in other repetitions of this experiment); (c) 5-diphenylhydroxysilyl-1-pentanal (fractions 39–70, chloroform–benzene), 2.63 g. (52%); and (d) 5-diphenylhydroxysilylpentanoic acid (fractions 76–85, chloroform), 0.35 g. (7.5%), m.p. 102–103° after recrystallization from cyclohexane. Details of the individual compounds follow.

5-Diphenylhydroxysilyl-1-pentanal.—Removal of the solvent from the chromatograph fractions gave an oil. It could not be crystallized and failed to yield a 2,4-dinitrophenylhydrazone. The compound failed to give a good analysis, presumably because it could not be purified adequately.

Anal. Calcd. for $C_{17}H_{20}OSi$: C, 71.9; H, 7.11. Found: C, 73.3; H, 7.31.

Treatment of 2.63 g. (0.0093 mole) of the aldehyde in 50 ml. of acetone at 0° with 4 ml. of an oxidizing mixture made up from 25.8 g. (0.25 mole) of 96% sulfuric acid and 16.7 g. (0.167 mole) of chromium trioxide and water to make 100 ml., added over 30 min. and stirred an additional 15 min. while warming to room temperature, gave on work-up and crystallization from cyclohexane 1.68 g. (61%) of 5-diphenylhydroxysilylpentanoic acid, m.p. 101–103°, identified by mixture melting point with the material isolated from the original chromatograph column.

5-Diphenylhydroxysilylpentanoic Acid.—Removal of the solvents from the chromatograph fractions gave an oil. This was purified by dissolving in aqueous sodium bicarbonate and extracting the organic impurities with ether. Acidification of the aqueous layer precipitated the acid which was taken up in ether and dried, and the ether was removed to give a slush which was recrystallized from cyclohexane to give 0.35 g. (7.5%) of acid, m.p. 102–103°. The infrared spectrum showed absorption at 2.70 (SiO–H), 3–4 (broad, COOH), and 5.81 μ (C=O).

Anal. Calcd. for $C_{17}H_{20}OSi$: C, 68.1; H, 6.74. Found: C, 68.4; H, 6.29.

1,1-Diphenylsila-2-cyclohexanone.—Removal of the solvents from the ketone fractions from the chromatograph gave 0.25 g. (5%) of ketone, which had a strong infrared absorption at 6.07 μ, but which was not pure, small peaks characteristic of the acid being present. In one case, when a chromatograph was carried out under N_2 using deoxygenated solvents, the ketone was relatively free of the acid impurities. This material gave infrared and ultraviolet spectra essentially the same as that of the crystalline material previously described but failed to crystallize. At this time in our investigations solid ketone had not yet been synthesized and seed crystals were not available.

Acid Stability of Diphenylsilacyclohexanone.—To a solution of 0.3 g. (0.0011 mole) of ketone in 4.8 ml. of acetone, maintained at 0° was added over 10 min. a solution of 0.05 ml. of 96% sulfuric acid in 3.2 ml. of water. The rapidly stirred mixture was allowed to warm to room temperature over 5 min. These conditions approximate very closely the acid conditions of the chromium trioxide oxidation. Work-up, by ether extraction, gave on evaporation a gum with an infrared spectrum essentially that of the original ketone and containing no bands at 2.7 or 3.7 μ characteristic of the aldehyde 11, although a weak carbonyl band, probably due to air oxidation, was observed at 5.77 μ. Recrystallization gave recovered ketone in good yield.

Reduction of Diphenylsilacyclohexanone to Diphenylsilacyclohexanol.—To 0.050 g. (0.00019 mole) of diphenylsilacyclohexanone, shown by infrared spectrum to be slightly contaminated with diphenylhydroxysilylpentanoic acid but free of diphenylcyclohexanol, was added 0.10 g. (0.0026 mole) of lithium aluminum hydride in 10 ml. of ether. After stirring overnight, careful hydrolysis and work-up gave an oil which was chromatographed on silica gel using carbon tetrachloride, 1:1 carbon tetrachloride–benzene, and benzene as eluents. From the benzene eluents was obtained a few drops of oil whose infrared spectrum was virtually identical with that of authentic 1,1-diphenylsila-2-cyclohexanol.

1,1-Diphenylsila-2-methyl-2-cyclohexanol.—Approximately 0.1 g. (0.0003 mole) of ketone in ether was treated with excess methylmagnesum bromide over 15 min. After work-up in the usual manner, evaporation of the dried ether extracts gave a few drops of viscous oil, whose infrared spectrum showed absorption at 2.78 μ (α-silylcarbinol). Chromatography on a short acid alumina column using benzene as eluent gave after evaporation of the solvent a clear, colorless viscous oil. The infrared spectrum showed absorption at 2.78 μ, and the n.m.r. showed a multiplet at $\delta = 7.1–7.6$ (aromatic), a broad band at 1.68 (CH_2), a singlet at 1.25 (CH_3), and a singlet at 0.85 p.p.m. (OH) which moved upfield on dilution. Integration showed the intensity ratio of these peaks at 10:7.6:3.2:1, in comparison with the preidcted 10:8:3:1 ratio.

Anal. Calcd. for $C_{18}H_{22}OSi$: C, 76.6; H, 7.80. Found: C, 75.7; H, 7.75.

Hydroboration and Oxidation of Vinyltriphenylsilane.—To a mixture of 0.89 g. (0.0236 mole) of sodium borohydride in 20 ml. of dry diglyme and 1.03 g. (0.0077 mole) of aluminum chloride in 30 ml. of dry diglyme was added 10 g. (0.035 mole) of vinyltriphenylsilane in 50 ml. of dry ether. The mixture was stirred at reflux for 3 hr. and then was carefully hydrolyzed with saturated ammonium chloride solution. The organic material was extracted with ether, the ether layers were dried, and the solvent was removed under reduced pressure. The residue was dissolved in tetrahydrofuran and 0.54 g. (0.0135 mole) of sodium hydroxide in 10 ml. of water was added, followed by 5.5 ml. of 30% hydrogen peroxide solution. The mixture became quite hot. After stirring for 18 hr., the mixture was acidified and extracted with ether. After drying and removal of the ether, the residue was dissolved in ethanol from which 0.25 g. (3%) of crystalline hexaphenyldisiloxane separated, m.p. 215–220°, identified by mixture melting point. The ethanol was removed under reduced pressure, and the residue was crystallized from cyclohexane, from which 4.35 g. (41%) of crystalline material was obtained, m.p. 91–97°. Recrystallization failed to alter the melting point. The infrared spectrum of the material showed bands at 2.78 and 11.32 μ, characteristic of 1-triphenylsilylethanol, and 2.76 and 10.84 μ, characteristic of 2-triphenylsilylethanol. Known mixtures of authentic 1- and 2-triphenylsilylethanols were prepared and the ratio of the peak heights at 11.32 and 10.84 μ were determined relative to the per cent composition of the mixtures. By comparing the ratio of the peak heights from the above mixture with this data it was established that this material contained about 80% 1-triphenylsilylethanol and 20% 2-triphenylsilylethanol.

Propionyltriphenylsilane.[7]—1-Triphenylsilylpropanol, m.p. 80–82°, was prepared in 37% yield by addition of triphenylsilyllithium to propionaldehyde. The infrared spectrum showed SiC–OH absorption at 2.78 μ.

Anal. Calcd. for $C_{21}H_{22}OSi$: C, 79.2; H, 6.96. Found: C, 79.0; H, 7.13.

To a solution of 5.45 g. of 1-triphenylsilylpropanol in 50 ml. of purified acetone was added dropwise over 30 min. 8.40 ml. of an oxidizing mixture made up from 25.8 g. (0.25 mole) of 96% sulfuric acid, 16.7 g. (0.167 mole) of chromium trioxide, and water to make 100 ml. The solution became green and separated into two layers. After 15-min. additional stirring, the acetone layer was removed, the aqueous layer was extracted with acetone, and the combined acetone layers were dried over magnesium sulfate. Removal of the acetone gave solid material which was crystallized from carbon tetrachloride to yield 3.05 g. (65%) of triphenylsilanol, m.p. 150–152°, identified by infrared spectrum and mixture melting point. Removal of the carbon tetrachloride from the mother liquor and crystallization of the residue from

95% ethanol gave 1.75 g. (33%) of propionyltriphenylsilane, m.p. 105–106°. The infrared spectrum showed carbonyl absorption at 6.08 μ.

Anal. Calcd. for $C_{21}H_{20}OSi$: C, 79.7; H, 6.37. Found: C, 79.1; H, 6.73.

Acknowledgment.—The support of part of this research by the National Research Council of Canada is gratefully acknowledged, as is the technical assistance of D. M. MacRae.

Pyrazolidinone Oxidation. The Oxidation of 1-Phenyl-4,4-dimethyl-3-pyrazolidinone in Alkaline Solution

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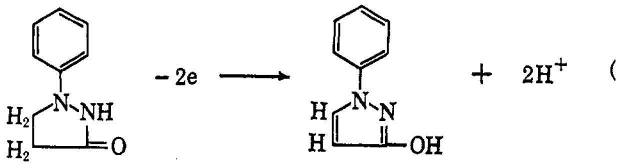
Received March 3, 1965

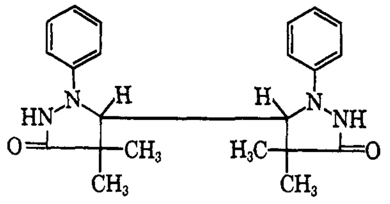
The oxidation of 1-phenyl-4,4-dimethyl-3-pyrazolidinone in alkaline solution was studied by a spectrophotometric method and also by product analysis. Under mild conditions the pyrazolidinone ring is cleaved to give benzene, nitrogen, isobutyraldehyde, CO_2, and a resinous polymeric material as major products, and small amounts of acetone, formaldehyde, and biphenyl. The reaction scheme proposed involves the formation of the pyrazolidinone semiquinone, followed by semiquinone dismutation which leads to the formation of an unstable, short-lived species which undergoes ring cleavage and produces isobutyraldehyde. The formation of other oxidation products is apparently due to further oxidation of the fragment that remains after the loss of isobutyraldehyde. The mechanism of oxidation which accounts for the major products is consistent with the observed stoichiometry, spectrochemical data, and the analytical results.

1-Phenyl-3-pyrazolidinone and its derivatives have become increasingly important as photographic developing agents. The mechanism of oxidation of the parent compound, 1-phenyl-3-pyrazolidinone, has been studied by several groups of workers.[1–4] The reaction is a two-step process in which two electrons and two protons are lost by the pyrazolidinone to form the very stable 1-phenyl-3-hydroxypyrazole (eq. 1). The existence of a resonance-stabilized semiquinone intermediate in this reaction has been shown by electrochemical[2] and by spectrophotometric measurements in the visible region of the spectrum.[5] Similar products are formed when the 4-alkyl-substituted derivatives of 1-phenyl-3-pyrazolidinone are oxidized. However, 4,4-dialkyl-substituted pyrazolidinones cannot undergo a similar transformation, since the carbon atom α to the carbonyl group carries no hydrogen atoms, although these compounds are easily oxidized by either silver ions or by other mild oxidizing agents.



(1)

No definitive study of the mechanism of oxidation of these 4,4-dialkyl-substituted compounds has appeared. Allen and Byers[6] theorized that a dimeric product, 5,5′-bis(4,4-dimethyl-1-phenyl-3-pyrazolidinone) (I) was formed upon oxidation. Jaenicke[7] has suggested that compounds of this type are oxidized in alkaline solution to a positively charged intermediate which adds water in a slow reaction to form a 5-hydroxypyrazolidinone compound, II. Recent studies in these laboratories, involving the measurement of optical properties of the steady-state condition in a flow system, have indicated that the initial steps in the oxidation of 1-phenyl-3-pyrazolidinone and 1-phenyl-4,4-dimethyl-3-pyrazolidinone are quite similar, although the subsequent reactions that follow semiquinone formation are quite different.



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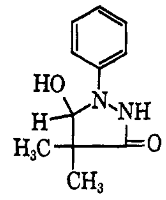

II

In this context, it was of interest to examine the products from the oxidation of the latter compound. The results are included in this paper. A detailed study of the kinetics of the oxidation of this class of compounds will be discussed in a subsequent paper.

Results

By the use of a rapid-flow technique in which the ultraviolet absorption spectrum of the steady state was recorded, the formation of a resonance-stabilized semiquinone intermediate in the oxidation of 1-phenyl-3-pyrazolidinone has been demonstrated (Figure 1). Dismutation of this semiquinone species, possibly followed by the formation of other short-lived reaction intermediates, leads ultimately to 1-phenyl-3-hydroxypyrazole as the final oxidation product. Experiments in which 1-phenyl-4,4-dimethyl-3-pyrazolidinone was oxidized under similar conditions show the formation of a semiquinone intermediate, which is even more stable than that formed from the unsubstituted compound. However, no clearly defined specific oxidation product is obvious from the examination of the ultraviolet absorption spectrum of a solution of the oxidized pyrazolidinone (Figure 2).

The oxidation of 1-phenyl-4,4-dimethyl-3-pyrazolidi-

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