(c) From *o*-Phenylenedilithium and Triphenylchlorosilane (Attempted).—An ethereal solution containing 0.014 mole of *o*-phenylenedilithium was added to 8.23 g. (0.028 mole) of triphenylchlorosilane in 100 ml. of ether. After adding 75 ml. of toluene, the ether was distilled, and the toluene solution heated at reflux for 24 hr. Work-up employing the usual chromatographic techniques gave an 11.7% yield of tetraphenylsilane, a 14.1% yield of hexaphenyldisiloxane and a 21.4% yield of triphenylsilanol, plus a resinous brown material.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

The Aluminum Chloride-catalyzed Intramolecular Cyclization of Some Organosilicon Compounds. Studies in the Benzosilacyclanone Series

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The series of silyl-substituted carboxylic acids $(C_6H_5)_3Si(CH_2)_nCOOH$ (n = 1, 2, 3) was prepared by oxidation of the corresponding carbinols. Whereas triphenylsilylacetic acid decomposed under acidic conditions, triphenylsilylpropionic acid and triphenylsilylbutyric acid could be converted to acid chlorides. On treatment of the latter with aluminum chloride in nitrobenzene, an intramolecular cyclization occurred giving rise to the corresponding benzosilacyclanones.

The Friedel–Crafts coupling of acyl halides with aromatic silicon compounds has been described as being of limited utility for the preparation of aromatic silicon-containing ketones because of the susceptibility of silicon–aromatic bonds toward cleavage by acidic reagents. The principal reaction of tetraphenylsilane in chloroform with aluminum chloride is that of cleavage, resulting in an 80% yield of silicon tetrachloride.[1] Similarly, tetrabenzylsilane under these conditions also gave silicon tetrachloride.[1] Attempts to acylate triethylphenylsilane in the presence of aluminum chloride yielded benzene, hexaethyldisiloxane and the corresponding ketone in which the triethylsilyl group had been replaced by the acyl group.[2]

Benkeser and Currie,[3] however, were able to acetylate 2-trimethylsilylthiophene and 2-trimethylsilylfuran with iodine as a catalyst. The *m*- and *p*-trimethylsilylbenzoyl chlorides acetylate toluene smoothly in the presence of aluminum chloride,[4] but the *o*-isomer does not. Similarly, anisole has been acylated by *p*-trimethylsilylbenzoyl chloride.[4] Acetyl fluoride has been found to acylate silicon-substituted phenyl compounds satisfactorily in the presence of boron trifluoride.[5]

These results encouraged our studies in preparing cyclic organosilicon compounds containing functional groups by intramolecular acylation reactions. So far, only a few organofunctional silacyclanes have been reported in the literature.[6-8] As our starting materials, the series of triphenylsilyl-substituted alcohols $(C_6H_5)_3Si(CH_2)_nOH$ (n = 2,3,4) was used. These compounds have been made readily available by cleavage of ethylene oxide,[9] trimethylene oxide[10] and tetrahydrofuran[11] with triphenylsilyllithium. Chromic acid oxidation[12] of these alcohols furnished the corresponding acids. Triphenylsilylacetic acid was obtained only in poor yield, probably due to its low stability under acidic conditions. This is in accord with the known fact[13] that carboxylic acids containing silicon in the α-position are easily hydrolyzed. 3-Triphenylsilylpropionic acid and 4-triphenylsilylbutyric acid were prepared in satisfactory yields. The latter compound was also obtained by an alternative approach: 3-triphenylsilylpropanol was converted to the bromide using phosphorus tribromide,[14] and the corresponding Grignard reagent treated with carbon dioxide.

When an attempt was made to convert triphenylsilylacetic acid to its acid chloride, which on subsequent treatment with aluminum chloride was expected to cyclize, the work-up yielded only triphenylsilanol. This again demonstrates the relative ease of cleavage of the Si–C bond in this acid. Under the same conditions, 3-triphenylsilylpropionic acid, when allowed to react with thionyl chloride, followed by aluminum chloride in nitrobenzene, afforded a 47.9% yield of the expected cyclic ketone I, 2:3-benzo-1,1-diphenyl-1-silacyclohexen-2-one-4 (or 2,3-dihydro-1,1-diphenyl-4H-

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(1) W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931).

(2) B. N. Dolgov and O. K. Panina, *Zhur. Obschei Khim.*, **18**, 1293 (1948) [*C. A.*, **43**, 2177 (1949)].

(3) R. A. Benkeser and R. B. Currie, THIS JOURNAL, **70**, 1780 (1948).

(4) R. A. Benkeser and H. R. Krysiak, *ibid.*, **76**, 599 (1954).

(5) H. H. Szmant and S. Skendrovich, *ibid.*, **76**, 2282 (1954).

(6) A. D. Petrov, G. I. Nikishin, N. P. Smetankina and Yu. P. Egerov, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, **5**, 861 (1955) [*C. A.*, **50**, 9282, 11230 (1956)].

(7) J. M. Hersh, U. S. Patent 2,615,033 (1952).

(8) R. A. Benkeser and E. W. Bennett, THIS JOURNAL, **80**, 5414 (1958).

(9) H. Gilman, D. Aoki and D. Wittenberg, *ibid.*, **81**, 1107 (1959).

(10) D. Wittenberg, D. Aoki and H. Gilman, *ibid.*, **80**, 5933 (1958).

(11) D. Wittenberg and H. Gilman, *ibid.*, **80**, 2677 (1958).

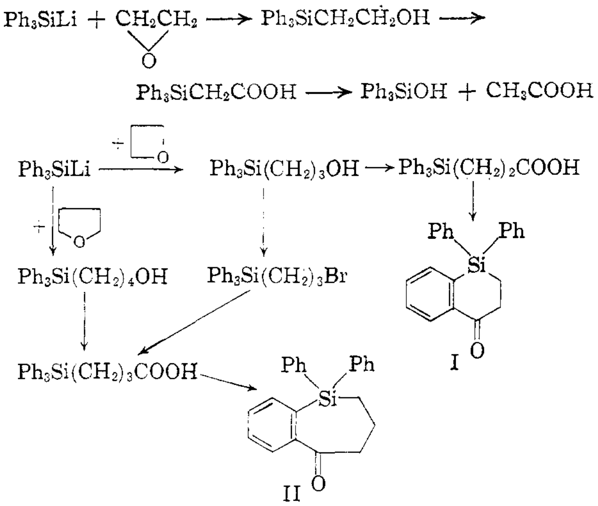
(12) Modification of the method of H. Gilman, C. G. Brannen and R. K. Ingham, *ibid.*, **78**, 1689 (1956); see also, D. W. Lewis and G. C. Gainer, *ibid.*, **74**, 2931 (1952).

(13) (a) H. Gilman and H. Hartzfeld, *ibid.*, **73**, 5878 (1951); (b) L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, *ibid.*, **71**, 1509 (1949); (c) F. C. Whitmore, L. H. Sommer, J. R. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

(14) Modification of the method of L. H. Sommer, R. E. Van Strien and F. C. Whitmore, *ibid.*, **71**, 3056 (1949); see also ref. 11.

1-silanaphthalen-4-one).[15] The corresponding cyclization of 4-triphenylsilylbutyric acid yielded 17.8% of 2:3-benzo-1,1-diphenyl-1-silacyclohepten-2-one-4 (II). Both ketones formed 2,4-dinitrophenylhydrazones. Additional confirmation of their structure was obtained from molecular weight determinations and from their infrared spectra.

To our knowledge, these are the first reported reactions in which a silyl-substituted benzene ring is acylated in an *o*-position using Friedel–Crafts catalysts.



Benkeser and Bennett[3] compared the cyanohydrin dissociation constants as well as the infrared spectra of 4,4-dimethyl-4-silacyclohexanone and its carbon analog and observed that the reactivity of the six-membered silicon ring approaches (albeit in a small way) the reactivity of the corresponding seven-membered carbon ring. Infrared spectra of a series of benzocyclanones recently have been determined.[13] Their carbonyl absorption frequencies agree well with those of the benzosilacyclanones I and II. The influence of the increased ring size, caused by replacement of a carbon atom by silicon, seems to be compensated by the influence of the diphenylsilylene group in an *o*-position to the carbonyl group (see Table I).

TABLE I

CARBONYL ABSORPTION FREQUENCIES OF SOME CYCLIC KETONES

Compound	λ_{max}, cm.$^{-1}$	Reference
Ketone I	1683	Present work
Ketone II	1680	Present work
Indanone-1	1723	16
Tetralone-1	1681	16
1:2-Benzocyclohepten-1-one-3	1676	16
1:2-Benzocycloöcten-1-one-3	1667	16
Acetophenone	1686	16
4,4-Dimethyl-4-silacyclohexanone	1702	8
4,4-Dimethylcyclohexanone	1709	8

An attempt to cyclize 3-triphenylsilylpropanol, using boron trifluoride in nitrobenzene as a catalyst, was unsuccessful. None of the expected 3,4-dihydro-1,1-diphenyl-2H-1-silanaphthalene was obtained. Instead, the catalyst caused rupture of the phenyl–silicon bonds. The same Si–C cleavage reaction was observed in an attempted cyclization of 3-triphenylsilylpropyl bromide, using ferric chloride as a catalyst.

Experimental[17]

Triphenylsilylacetic Acid.—To a stirred solution of 6.08 g. (0.02 mole) of 2-triphenylsilylethanol[9] in 75 ml. of glacial acetic acid, 5 g. (0.05 mole) of chromic acid was added in small portions at 25°. The mixture then was stirred for 2 hours at 25–30°, and subsequently poured on crushed ice. The suspension was extracted with ether, the organic solution washed with water and then extracted with cold 2% sodium hydroxide solution. Acidification of the alkaline solution at 0° with dilute hydrochloric acid gave 1.3 g. (20%) of a white solid, m.p. 165–170°. Several recrystallizations from a benzene–cyclohexane mixture raised the melting point to 177–177.5°.

Anal. Calcd. for $C_{20}H_{18}O_2Si$: Si, 8.82; neut. equiv., 318.2. Found: Si, 8.77, 8.78; neut. equiv., 323.7.

From the ethereal solution, 3.3 g. (60%) of triphenylsilanol, m.p. and mixed m.p. 155–156°, was isolated.

3-Triphenylsilylpropionic Acid.—To a solution of 15.9 g. (0.05 mole) of 3-triphenylsilylpropanol-1[10] in 150 ml. of glacial acetic acid, 12 g. (0.12 mole) of chromic acid was added in small portions. During the addition, the temperature of the continuously stirred mixture was maintained at 30–32°. Subsequent to stirring for 3 hours at 45–46°, the dark solution was poured in a thin stream on crushed ice. The greenish-white solid was collected and washed with water. It was then dissolved in ether and the organic solution again washed several times with water. Extraction with 2% aqueous sodium hydroxide, followed by acidification with dilute hydrochloric acid, gave 9.0 g. (54%) of 3-triphenylsilylpropionic acid, m.p. 144–145°. Recrystallization from a mixture of ethyl acetate and petroleum ether (b.p. 60–70°) raised the melting point to 145–146°. The experiment was checked twice.

Anal. Calcd. for $C_{21}H_{20}O_2Si$: Si, 8.45; neut. equiv., 332.5. Found: Si, 8.47, 8.56; neut. equiv., 332.

2:3-Benzo-1,1-diphenyl-1-silacyclohexen-2-one-4 (2,3-Dihydro-1,1-diphenyl-4H-1-silanaphthalen-4-one).—Two grams (0.0063 mole) of 3-triphenylsilylpropionic acid was refluxed gently for 45 min. with 10 ml. of thionyl chloride. The excess reagent was removed by distillation under reduced pressure. The last traces of thionyl chloride were removed by co-distillation with two 10-ml. portions of benzene. The resulting crude acid chloride was dissolved in 25 ml. of nitrobenzene and 0.85 g. (0.0065 mole) of aluminum chloride was added in three portions at room temperature with continuous stirring. The mixture was stirred at room temperature for 30 minutes and subsequently hydrolyzed with dilute iced hydrochloric acid. After addition of some ether, the organic layer was separated and the aqueous layer extracted with three 30-ml. portions of ether. The combined extracts were dried with sodium sulfate and the ether removed by distillation. The residual nitrobenzene solution was chromatographed on alumina (100 g., 80–200 mesh). Elution with petroleum ether gave only nitrobenzene. Using benzene as an eluent, 0.9 g. (47.9%) of ketone I was obtained, m.p. 124.5–127°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the melting point to 127–128°.

Anal. Calcd. for $C_{21}H_{18}OSi$: Si, 8.92; mol. wt., 314.4. Found: Si, 8.79, 8.85; mol. wt. (Rast), 295.

When in a second experiment the cyclization of the acid chloride was carried out in a mixture of nitrobenzene and cyclohexane (1:1), the same work-up gave the cyclic ketone I in a 38.5% yield.

The ketone formed a 2,4-dinitrophenylhydrazone, m.p. 240° dec.

Anal. Calcd. for $C_{27}H_{22}N_4O_4Si$: C, 65.57; H, 4.49; N, 11.33. Found: C, 65.37, 65.50; H, 4.45, 4.45; N, 11.43, 11.45.

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[15] The names and the numbering system used herein are those recommended by the editorial staff of "Chemical Abstracts."

[16] W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **77**, 4172 (1955).

[17] Melting points are uncorrected. Silicon analyses were carried out according to the method of H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, *ibid.*, **72**, 5767 (1950).

Samples of the ketone I have been reduced by lithium aluminum hydride in tetrahydrofuran and in an ether-benzene mixture. The reaction product in each case was a viscous oil, which could not be crystallized. Attempts to convert the crude reduction product into a *p*-toluenesulfonyl derivative also were unsuccessful.

3-Triphenylsilylpropylbromide.—A mixture of 10 g. (0.0314 mole) of 3-triphenylsilylpropanol-1 and 5.4 g. (0.02 mole) of phosphorus tribromide was placed in a Schlenk tube and heated for 12 hr. on a steam-bath. Benzene was then added and the mixture hydrolyzed with cold water. After washing the organic layer several times with water, dilute ammonium hydroxide and dilute sulfuric acid, it was filtered and the solvent removed. The residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. The product, eluted with the same solvent, was recrystallized from ethanol to give 6.8 g. (57%) of 3-triphenylsilylpropyl bromide, m.p. 92–93°.

Anal. Calcd. for $C_{21}H_{21}BrSi$: Si, 7.36. Found: Si, 7.24, 7.36.

4-Triphenylsilylbutyric Acid. (A) **From 4-Triphenylsilylbutanol-1.**—To a stirred solution of 4-triphenylsilylbutanol-1[11] in 75 ml. of glacial acetic acid, 5 g. (0.05 mole) of chromic acid was added in small portions at 30–32°. The resulting mixture was stirred for 3 hours at 45–46° and subsequently worked up in the same manner as described for 3-triphenylsilylpropionic acid. There was obtained 5.0 g. (73.5%) of 4-triphenylsilylbutyric acid, m.p. 165–167°. Several recrystallizations from a mixture of ethyl acetate and petroleum ether (b.p. 60–70°) raised the melting point to 171–172°.

Anal. Calcd. for $C_{22}H_{22}O_2Si$: Si, 8.09; neut. equiv., 346.4. Found: Si, 8.07, 8.24; neut. equiv., 354.1.

(B) **From 3-Triphenylsilylpropyl Bromide.**—A Grignard reagent was prepared from 1.3 g. (0.0036 mole) of triphenylsilylpropyl bromide and 0.1 g. of magnesium in 50 ml. of ether. The mixture was carbonated with Dry Ice. The work up in the usual manner yielded 0.1 g. of crude acid. Two recrystallizations from a mixture of ethyl acetate and petroleum ether (b.p. 60–70°) gave needles melting at 172–173°. A mixture melting point with the product prepared by method A was undepressed.

2:3-Benzo-1,1-diphenyl-1-silacyclohepten-2-one-4 (II).—A mixture of 1.5 g. (0.0045 mole) of 4-triphenylsilylbutyric acid and 10 ml. of thionyl chloride was refluxed gently for one hour. Excess thionyl chloride was removed under reduced pressure, the last traces of the reagent by co-distillation with two 10-ml. portions of benzene. The crude acid chloride was dissolved in 15 ml. of nitrobenzene and, with cooling in an ice-bath, 0.60 g. (0.045 mole) of aluminum chloride was added. The mixture was stirred for 30 minutes at room temperature, subsequently hydrolyzed and worked up as described before. On chromatography with alumina, the benzene eluate yielded a small quantity of a viscous oil, which crystallized on treatment with methanol. There was obtained 0.25 g. (17.8%) of ketone II, m.p. 103–105°. Recrystallization from a mixture of methanol and ether raised the melting point of the product to 105–106°.

Anal. Calcd. for $C_{22}H_{20}OSi$: C, 80.42; H, 6.14. Found: C, 80.20, 80.13; H, 6.30, 6.26.

The ketone II gave a semicarbazone, m.p. 177–178°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF RHODE ISLAND, KINGSTON, R. I.]

The Free Radical Addition of Hydrogen Bromide to the 1-Bromocycloalkenes[1]

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The addition of hydrogen bromide to 1-bromocyclobutene, 1-bromocyclopentene and 1-bromocycloheptene under free radical conditions gives ratios of *cis* to *trans* isomers of the 1,2-dibromocycloalkanes of 79:21, 94:6 and 91:9, respectively. These isomers have been separated and characterized. An explanation of the variation in isomer ratios is given in terms of a balance between a mechanistic preference for a *trans* addition process and a steric inhibition to the formation of the *cis* isomers.

Introduction

A tendency toward a *trans* mechanism in the free radical addition of hydrogen bromide to olefins has been observed in a substantial and growing number of cases. Among these are the additions to 1-bromocyclohexene,[2] 1-methylcyclohexene,[2] 1-methylcyclopentene,[3] 1-methylcycloheptene,[4] 1-chlorocyclohexene,[5] *cis*- and *trans*-2-bromo-2-butene,[6] propyne[7] and (using deuterium bromide) *cis*- and *trans*-2-butene.[8] Many of these tests for a stereospecific mechanism have been carried out on cyclic olefins in order to avoid the complications of *cis*-*trans* isomerization prior to addition. However, the reaction has shown a high degree of stereospecificity in all of the compounds investigated with the exception of 2-bromo-2-norbornene, where the bridged ring structure introduces major steric complications.[9] Of the olefins studied, only 1-bromocyclohexene has been demonstrated to show an almost completely stereospecific path in the addition, yielding *cis*-1,2-dibromocyclohexane contaminated with only 0.3% of the *trans* isomer.[5] It appeared likely to us that this reaction constitutes a special case in that the cyclohexane ring is unique among the simple ring systems in the arrangement of its bonds in axial and equatorial types. Although the steric and mechanistic dif-

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[2] H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

[3] King Howe, Ph. D. thesis, University of Wisconsin, 1957.

[4] Bruce Bohm, M. S. thesis, University of Rhode Island, 1958.

[5] H. L. Goering and L. L. Sims, THIS JOURNAL, **77**, 3465 (1955).

[6] H. L. Goering and D. W. Larsen, *ibid.*, **79**, 2653 (1957).

[7] P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

[8] P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).

[9] N. A. LeBel, Abstracts of Papers of American Chemical Society Meeting, Boston, Mass., April, 1959, p. 4-O.