[CONTRIBUTION FROM THE RESEARCH DIVISION, WYANDOTTE CHEMICALS CORP.]

Ferrocenes. III. Unsymmetrically Disubstituted Siloxanylferrocenes[1,2]

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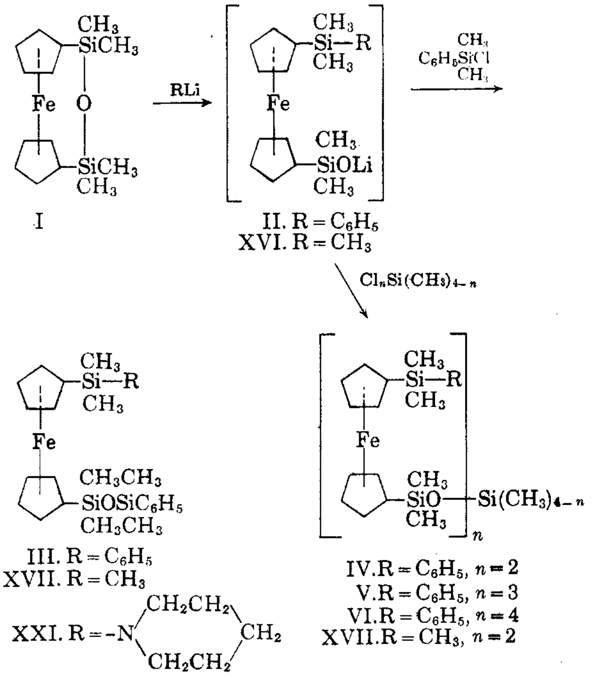
Cleavage of the siloxane linkage in the bridged compound 1,3-(1,1′-ferrocenylene)-1,1,3,3-tetramethyldisiloxane with phenyllithium, methyllithium, and 1-piperidyllithium yielded intermediates which, when treated *in situ* with chlorosilanes, furnished a number of heteroannularly disubstituted siloxanylferrocenes. The infrared spectra of these compounds were examined, and exceptions to the 9–10 rule have been attributed to the presence of phenylsilyl groups.

As part of a program on the preparation of thermally stable fluids, the syntheses of a number of symmetrically disubstituted siloxanylferrocenes have been reported from this laboratory.[3,4] The work now has been extended to include the preparation of heteroannularly disubstituted siloxanylferrocenes in which the group on one cyclopentadiene ring differs from that on the other.

Two general methods reported in the literature[3–7] for the synthesis of silicon-containing ferrocenes involved either treatment of a mixture of mono- and dilithioferrocene with a chlorosilane, or conversion of a silicon-containing cyclopentadiene to the corresponding ferrocene. These methods did not seem suitable for the preparation of unsymmetrically disubstituted ferrocenes, inasmuch as a mixture of products can be expected if there were employed two different chlorosilanes in the former instance or two differently substituted cyclopentadienes in the latter.

It appeared that the desired unsymmetrical compounds might be synthesized *via* cleavage of the siloxane bridge in 1,3-(1,1′-ferrocenylene)-1,1,3,3-tetramethyldisiloxane (I) a compound reported previously.[4] Gilman and co-workers[8] have described the cleavage of hexaphenyldisiloxane by phenyllithium to yield tetraphenylsilane (80%) and lithium triphenylsilanolate, isolated as the silanol (79%). If applied to the above bridged ferrocene, cleavage by phenyllithium should yield an intermediate readily convertible by chlorosilanes to unsymmetrically disubstituted siloxanylferrocenes. This route was attractive in that it should permit the synthesis of unsymmetrically disubstituted ferrocene derivatives without the necessity for additional clarification of the heteroannular or homoannular nature of the product. This point is particularly significant in the synthesis of phenylsilylferrocenes, wherein the usual method for distinguishing heteroannular from homoannular substitution is unreliable (see discussion of infrared studies below).

The reaction of the bridged ferrocene, I, with phenyllithium in ether and treatment of the resulting solution with phenyldimethylchlorosilane furnished the desired 1-phenyldimethylsilyl-1′-(3-phenyl - 1,1,3,3 - tetramethyldisiloxanyl)ferrocene (III) in 65% yield. To our knowledge, this is the first instance of the preparation of a disubstituted ferrocene *via* cleavage of a bridged ferrocene.



I

II. R = C_6H_5
XVI. R = CH_3

III. R = C_6H_5
XVII. R = CH_3
XXI. R = $-N(CH_2CH_2)_2CH_2$

IV. R = C_6H_5, $n = 2$
V. R = C_6H_5, $n = 3$
VI. R = C_6H_5, $n = 4$
XVII. R = CH_3, $n = 2$

It should be noted that attack on the siloxane linkage in I occurred in preference to ring lithiation, whereas lithiation of ferrocene by butyllithium afforded a mixture of mono- and dilithioferrocene.[5]

Treatment of the unisolated intermediate silanolate, II, with dimethyldichlorosilane, methyl-

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[1] Presented at the Frederick F. Blicke Symposium of the Division of Medicinal Chemistry at the 138th National Meeting of the American Chemical Society, New York City, N. Y., September 1960.

[2] This investigation was conducted under contract with Materials Laboratory, Wright Air Development Division, Dayton, Ohio.

[3] Robert L. Schaaf, Peter T. Kan, Carl T. Lenk, and Eva P. Deck, *J. Org. Chem.*, **25**, 1986 (1960).

[4] Robert L. Schaaf, Peter T. Kan, and C. T. Lenk, *J. Org. Chem.*, **26**, 1790 (1961).

[5] R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954).

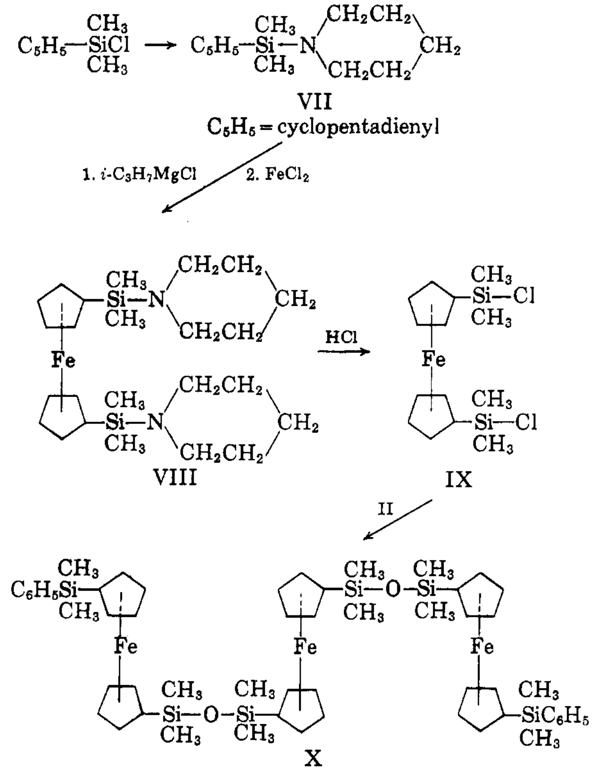
[6] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

[7] S. I. Goldberg, D. W. Mayo, M. Vogel, H. Rosenberg, and M. Rausch, *J. Org. Chem.*, **24**, 824 (1959).

[8] H. Gilman, H. N. Benedict, and H. Hartzfeld, *J. Org. Chem.*, **19**, 419 (1954).

trichlorosilane, and tetrachlorosilane gave 1,5-bis(1′-phenyldimethylsilyl-1-ferrocenyl)-1,1,3,3,5,5-hexamethyltrisiloxane (IV), tris[(1′-phenyldimethylsilylferrocenyl)dimethylsiloxy]methylsilane (V), and tetrakis[(1′ - phenyldimethylsilylferrocenyl)dimethylsiloxy]silane (VI), respectively, in yields from 37 to 55%.

Similarly, treatment of II with bis(dimethylchlorosilyl)ferrocene (IX) produced 1,1′-bis[3-(1′-phenyldimethylsilylferrocenyl)-1,1,3,3-tetramethyldisiloxanyl]ferrocene (X), a liquid which contained three ferrocene nuclei. The previously undescribed bis(dimethylchlorosilyl)ferrocene (IX) was prepared in crude form by a series of reactions involving reaction of cyclopentadienyldimethylchlorosilane with piperidine, and conversion of the resulting cyclopentadienyldimethyl(1-piperidyl)-silane (VII) to the corresponding ferrocene VIII, followed by treatment of VIII with hydrogen chloride.



VII

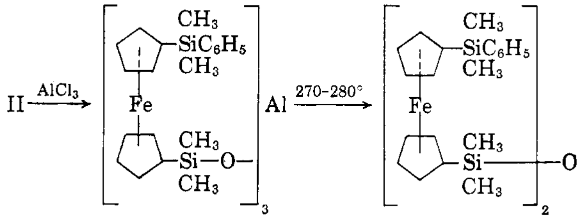
C_5H_5 = cyclopentadienyl

VIII

IX

X

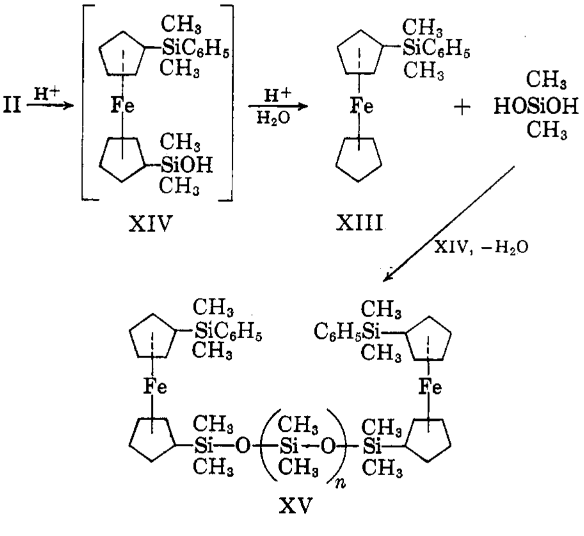
An attempt was made to prepare a siloxyaluminum compound, XI, by treatment of the intermediate silanolate, II, with aluminum chloride, but the product isolated did not contain aluminum. It was reported recently by Woods and Iverson[9] that tris(trimethylsiloxy)aluminum, which is analogous to XI, decomposed at 260 to 280° to produce 0.5 mole of hexamethyldisiloxane. Inasmuch as isolation of XI involved distillation at 270 to 280°, it is not surprising that the compound isolated was actually the disiloxane, XII. Presumably the desired reaction had taken place, but attempted distillation of the product had caused decomposition to XII.



XI

XII

Prior to this last experiment, the preparation of XII was attempted by the hydrolysis of II with aqueous ammonium chloride. The major product was, however, a monosubstituted ferrocene, phenyldimethylsilylferrocene (XIII). Apparently the silanol XIV, formed from II, was unstable in aqueous ammonium chloride, the ferrocenyl-silicon bond was broken, and XIII was formed, along with dimethylsilanediol. Formation of this diol was suggested by the isolation of a mixture of siloxanes, XV, which would arise from condensation of the diol with the intermediate silanol XIV. Analysis indicated n in XV to be between 2 and 3. It was initially surprising that such mild conditions resulted in extensive hydrolysis of the ferrocenyl-silicon bond; by contrast, the addition of sodium phenyldimethylsilanolate to a mixture of ether, water, and acetic acid gave phenyldimethylsilanol in 95% yield.[10] Studies of *para*-substituted trimethylarylsilanes have shown that the ease of cleavage of the aryl-silicon bond by an acidic reagent is facilitated when the aryl group is capable of furnishing a high electron density at the aryl-



XIV

XIII

XV

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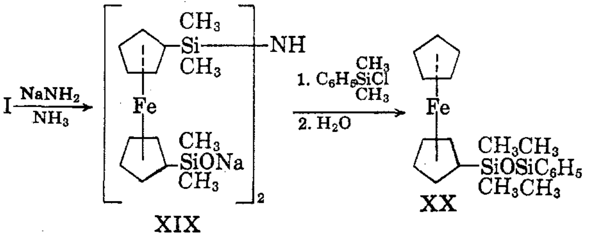
[9] W. G. Woods and M. L. Iverson, paper presented at the 136th National ACS Meeting, Atlantic City, N. J., September 1959.

[10] J. F. Hyde, O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. P. Roche, *J. Am. Chem. Soc.*, **75**, 5615 (1953).

silicon bond.[11-13] The ability of ferrocene to provide sites of high electron density is amply demonstrated by the considerably greater reactivity of ferrocene compared with benzene in electrophilic substitution processes.[14] In retrospect, then, it is logical that the ferrocene-silicon bond should be broken much more readily than the phenyl-silicon bond by acidic reagents.

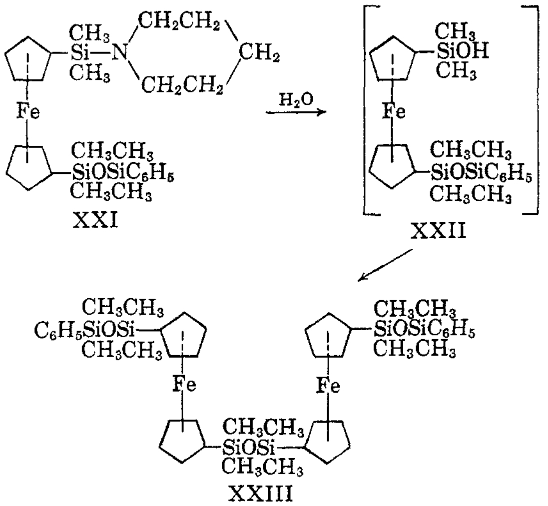
Although the cleavage of hexaphenyldisiloxane, as described by Gilman and co-workers, had proceeded in excellent yield with phenyllithium, no cleavage was detected with methyllithium under similar conditions.[8] In spite of this apparent lower reactivity, reaction of methyllithium over extended time periods with the bridged ferrocene, I, brought about the desired cleavage. Subsequent treatment of the intermediate silanolate, XVI, with phenyldimethylchlorosilane and dimethyldichlorosilane gave the expected products, 1-trimethylsilyl-1′-(3-phenyl-1,1,3,3-tetramethyldisiloxanyl)ferrocene (XVII) and 1,5-bis(1′-trimethylsilylferrocenyl)-1,-1,3,3,5,5-hexamethyltrisiloxane (XVIII) in 52% and 37% yields, respectively. According to the mechanism of the reaction of siloxanes with bases, as postulated by Hurd and co-workers,[15] it should be more difficult to cleave an alkylarylsiloxane (such as I) than a completely aryl-substituted siloxane, if electronic effects alone are considered. The fact that cleavage of I occurs suggests either that the siloxane bridge is strained, or that there is present a favorable steric arrangement in which siloxane linkages are susceptible to attack.

Sodamide has also been employed successfully to cleave a siloxane linkage. From the reaction of hexamethyldisiloxane with sodamide in liquid ammonia, Hyde and co-workers[10] obtained sodium trimethylsilanolate in 80% yield, along with hexamethyldisilazane. This reaction appeared attractive for application to the bridged ferrocene (I), inasmuch as the intermediate XIX would contain two reactive functional groups: the sodium silanolate group for treatment with chlorosilanes, and the silazane linkage for hydrolysis to a siloxane. Therefore, I was treated with sodamide in liquid ammonia, and the product, which by analogy would be XIX, was treated *in situ* with phenyldimethylchlorosilane. The product was not distilled, but was treated with water in an effort to convert the silazane linkage to a siloxane. Ammonia was evolved, but the product isolated was a crude monosubstituted compound, 1-ferrocenyl-3-phenyltetramethyldisiloxane (XX), obtained in 49% yield. The logical intermediate in the final step, a ferrocenylsilanol, was (as in the case of XIV) apparently unstable in the presence of aqueous ammonium chloride. Although only water was added, ammonium chloride could arise from hydrolysis of both the unchanged phenyldimethylchlorosilane and the silazane.



XIX XX

In this sequence, essentially four reactions were carried out prior to isolation of a product. In order to simplify the sequence, 1-piperidyllithium in ether was used in place of sodamide in liquid ammonia in the initial cleavage step. Subsequent addition of phenyldimethylchlorosilane furnished the desired piperidylsilyl compound, XXI, in 49% yield. Compound XXI reacted readily with water to give, in 82% yield, 1,3-bis[1′-(3-phenyltetramethyldisiloxanyl)ferrocenyl]tetramethyldisiloxane (XXIII), which contained two ferrocene nuclei and three disiloxane linkages. It is interesting to note that the intermediate ferrocenylsilanol, XXII, which was formed in the reaction with water, did not undergo hydrolysis of the ferrocenyl-silicon bond. The cleavage encountered previously therefore probably was due to the acidic conditions, and steric factors likely did not play a significant role.



XXI XXII

XXIII

The infrared spectra of a number of these disubstituted siloxanylferrocenes showed bands at 9 and 10 μ, which are usually indicative of monosubstitution. The 9–10 rule as set forth by Rosenblum and Woodward states that ferrocene derivatives, in which at least one ring remains unsubstituted, exhibit absorption in the infrared near 9 or 10 μ, while those derivatives in which both rings

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(11) R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **75**, 4528 (1953).

(12) H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

(13) C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 4449 (1957).

(14) See M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959), and references cited therein.

(15) D. T. Hurd, R. C. Osthoff, and M. L. Corrin, *J. Am. Chem. Soc.*, **76**, 249 (1954).

are either singly or multiply substituted do not exhibit such absorption.[16] Although it was recognized[16] that heteroannularly disubstituted compounds might show this absorption, if the substituents themselves were responsible for it, only one compound was known to violate the rule.[17] In the field of silicon-substituted ferrocenes, Goldberg and co-workers[7] have recently reported that the infrared spectrum of 1,1′-bis(tri-*n*-hexylsilyl)ferrocene showed strong bands at 9 and 10 μ, but they proved that the absorption was caused by the substituents.

In the course of our investigations, the infrared spectra of fifteen heteroannularly disubstituted ferrocenes were found to have bands at 9 and 10 μ, in violation of the 9–10 rule. The positions of the absorption bands in the 9 and 10 μ region in the infrared for twelve of these compounds are listed in Table I. It is significant that all the heteroannularly disubstituted ferrocenes which have bands near 9 and 10 μ contained phenylsilyl groups, and it is believed that these groups are responsible for the absorption. Analogous siloxanylferrocenes which did not contain phenylsilyl groups did not show absorptions near 9 and 10 μ. Furthermore, the spectrum of the simple monosubstituted compound, phenyldimethylsilylferrocene (XIII), showed two pairs of bands at 9 and 10 μ; only one pair can be attributed to monosubstitution; the other pair must be due to the presence of the phenyldimethylsilyl group. Bellamy lists an absorption caused by phenyl-silicon bonds near 9 μ.[18] In view of the fifteen exceptions, then, the 9–10 rule cannot be used reliably to eliminate heteroannular disubstitution, when one of the substituents contains a phenylsilyl group.

TABLE I

INFRARED SPECTRA

Compound	Infrared Absorption[a] at	
	9 μ	10 μ
III	8.95 s	10.02 m
IV	9.00 s	10.00 w
V	8.98 s	10.00 m (shoulder)
VI	9.00 s	9.90 m
X	8.98 m	10.00 w (shoulder)
XII	8.99 s	10.00 m (shoulder)
XIII	9.01 s; 9.04 s	9.98 m; 10.03 m
XVII	8.92 s	10.02 m
XVIII	—	—
XX	8.94 s; 9.03 m	10.02 m
XXIII	8.92 s	10.01 m
XXIV[b]	8.90 s	10.00 m
XXV[c]	8.90 s	10.01 m

[a] Intensities are noted as s (strong), m (medium), and w (weak). [b] 1,1′-Bis(3-phenyl-1,1,3,3-tetramethyldisiloxanyl)-ferrocene.[3] [c] 1,1′-Bis(5-phenyl-1,1,3,3,5,5-hexamethyltrisiloxanyl)ferrocene.[3]

EXPERIMENTAL[19]

Crude lithium (1′-phenyldimethylsilyl-1-ferrocenyl)dimethylsilanolate (II) *in solution.* Phenyllithium was prepared by the addition of 9.9 g. (0.063 mole of bromobenzene in 20 ml. of ether to 1.0 g. of lithium slices in 50 ml. of ether during a 1-hr. period, with an additional 1-hr. reflux to assure complete reaction. The phenyllithium solution was added to 20 g. (0.063 mole) of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (I) in 250 ml. of ether, and the mixture was refluxed overnight. This solution was employed for reactions of lithium (1′-phenyldimethylsilyl-1-ferrocenyl)-dimethylsilanolate (II) as described below.

1-Phenyldimethylsilyl-1′-(3-phenyl-1,1,3,3-tetramethyldisiloxanyl)ferrocene (III). To an ether solution of lithium (1′-phenyldimethylsilyl-1-ferrocenyl)dimethylsilanolate (II) prepared as described above was added 10.7 g. (0.063 mole) of phenyldimethylchlorosilane[20] in 50 ml. of ether. The mixture was stirred overnight, filtered, and solvent removed from the filtrate *in vacuo.* Distillation of the residue yielded two fractions, 5.5 g., b.p. 76–91°/0.1 mm., and 26 g., b.p. 207–230°/0.05 mm. By crystallization of the first fraction from isopropyl alcohol, 2.3 g. (11.5%) of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (I), m.p. 82–84°, was recovered. The second fraction upon redistillation yielded 21.5 g. (65%) of 1-(phenyldimethylsilyl)-1′-(3-phenyltetramethyldisiloxanyl)ferrocene (III), b.p. 200–208°/0.03 mm., n_D^{25} 1.5740.

Anal. Calcd. for $C_{28}H_{36}FeOSi_3$: C, 63.61; H, 6.86; Fe, 10.56. Found: C, 63.74, 63.81; H, 6.86, 6.91; Fe, 10.77.

1,5-Bis(1′-phenyldimethylsilyl-1-ferrocenyl)-1,1,3,3,5,5-hexamethyltrisiloxane (IV). Lithium (1′-phenyldimethylsilyl-1-ferrocenyl)dimethylsilanolate (II) was prepared in ether solution as described above, except that a 1.1:1 ratio of bromobenzene to the bridged compound was used. To the solution was added 4.1 g. (0.0318 mole) of dimethyldichlorosilane in 20 ml. of ether, and the mixture was stirred overnight. After filtration, solvent was removed under vacuum; the residue was extracted with petroleum ether, and the extract was distilled. From a fraction b.p. 73–160°/0.08 mm., 1.55 g. (8%) of I, m.p. 80–82°, was recovered by recrystallization from isopropyl alcohol. The largest fraction, 19.5 g. b.p. 284–319°/0.08 mm., was redistilled to give 14.5 g. (55%) of 1,5-bis(1′-phenyldimethylsilyl-1-ferrocenyl) hexamethyltrisiloxane (IV), b.p. 283–285°/0.03 mm., n_D^{25} 1.5791.

Anal. Calcd. for $C_{42}H_{56}Fe_2O_2Si_5$: C, 59.55; H, 6.90; Fe, 13.22. Found: C, 59.96; H, 7.15; Fe, 13.39, 13.34.

Tris[(1′-phenyldimethylsilylferrocenyl)dimethylsiloxy]-methylsilane (V). A solution of phenyllithium was prepared by the addition of 12.0 g. (0.077 mole) of bromobenzene in 30 ml. of ether to 1.0 g. of lithium slices in 50 ml. of ether during a 1-hr. period, with an additional 1-hr. reflux to assure complete reaction. The phenyllithium solution was added to 20 g. (0.063 mole) of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (I) in 250 ml. of ether, and the mixture was refluxed overnight. To this mixture was added 3.0 g. (0.021 mole of methyltrichlorosilane in 50 ml. of ether. The mixture

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(16) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

(17) K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *J. Am. Chem. Soc.*, **79**, 3420 (1957).

(18) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1958, 2nd ed., p. 334.

(19) All melting points and boiling points are uncorrected. Analysis for iron[4] was performed in this laboratory by Mr. Peter A. Marsh. Other analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y. Infrared spectra were obtained with a Baird Infrared Recording Spectrophotometer. Distillations were in general performed under nitrogen.

(20) Technical grade; Dow Corning Corporation, Midland, Mich. Other chlorosilanes were purchased from General Electric Corporation, Waterford, N. Y.

was stirred overnight at room temperature, filtered and solvent removed from the filtrate *in vacuo*. The residue was extracted with petroleum ether and the extract evaporated. Distillation of the residue gave a fraction, b.p. 80–100°/0.2 mm., from which 2.6 g. (13%) of I, m.p. 86–87°, was recovered by recrystallization from methanol. A second fraction, b.p. 270–276°/0.14 mm., was shown by analysis to be crude V (9.4 g., 37%). It was further purified by redistillation, b.p. 273–280°/0.06 mm.

Anal. Calcd. for $C_{61}H_{78}Fe_3O_2Si_7$: C, 59.89; H, 6.43; Fe, 13.69. Found: C, 60.21, 60.27; H, 6.49, 6.40; Fe, 13.96.

Tetrakis [(1′-phenyldimethylsilylferrocenyl)dimethylsiloxy] silane (VI). The preceding procedure was employed with the same quantities except that 2.72 g. (0.016 mole) of tetrachlorosilane was used in place of 0.021 mole of methyltrichlorosilane. After addition of the chlorosilane, the mixture was refluxed overnight. From a fraction b.p. 78–170°/0.25 mm., 4.3 g. (22%) of I, m.p. 86–88°, was recovered by recrystallization. Compound VI was collected in two fractions: 6 g., b.p. 270–286°/0.3 mm., and 5.0 g., b.p. 286–287°/0.3 mm.: total yield, 44%. The 5-g. fraction was analyzed.

Anal. Calcd. for $C_{80}H_{100}Fe_4O_4Si_9$: C, 59.98; H, 6.29; Fe, 13.95. Found: C, 60.00, 60.12; H, 6.53, 6.45; Fe, 13.84.

Cyclopentadienyldimethyl(1-piperidyl)silane (VII). Cyclopentadienyldimethylchlorosilane[3] (100 g.; 0.63 mole) in 700 ml. of ether was stirred under nitrogen in an ice bath while a solution of 107 g. (1.26 mole) of piperidine in 200 ml. of ether was added during a 15-min. period. After the mixture had stirred overnight at room temperature, the piperidine hydrochloride was removed by filtration and washed with petroleum ether. Solvent was removed from the filtrate and washings *in vacuo* under nitrogen, below room temperature. Distillation of the residue gave the desired VII in 82% yield, b.p. 56–60°/0.3 mm.

Anal. Calcd. for $C_{12}H_{21}NSi$: C, 69.49; H, 10.21; N, 6.75; Si, 13.55. Found: C, 68.62, 68.74; H, 10.48, 10.42; N, 7.01, 7.07; Si, 13.96, 14.21.

1,1′-Bis[dimethyl(1-piperidyl)silyl]ferrocene (VIII). An isopropylmagnesium chloride solution was prepared by dropwise addition of 125 ml. of isopropyl chloride to 26 g. (1.07 g.-atoms) of magnesium in 200 ml. of ether after the reaction had been initiated by a mixture of 5 ml. of isopropyl bromide and 25 ml. of isopropyl chloride. A solution of 200 g. (0.964 mole) of cyclopentadienyldimethyl(1-piperidyl)silane (VII) in 600 ml. of tetrahydrofuran was stirred under nitrogen in an ice bath while the isopropylmagnesium chloride solution was added during a 5-min. period. After the mixture was stirred for 6 hr. in bath, a ferrous chloride solution, prepared[21] from 52.8 g. of ferric chloride and 9.04 g. of iron powder in 200 ml. of tetrahydrofuran, was added in four portions, followed by 600 ml. of tetrahydrofuran. The ice bath was removed and the mixture was stirred overnight. Solvent was removed by evaporation *in vacuo* and the residue was extracted with petroleum ether (b.p. 30–60°). Vacuum evaporation of the extract and subsequent distillation gave 155 g. (69%) of VIII, b.p. 190–204°/0.38 mm.

When the period of reaction between the isopropylmagnesium chloride and VII was 1.5 hr., the yield of VIII, b.p. 187–195°/0.08 mm., n_D^{25} 1.5556, was 22%.

Anal. Calcd. for $C_{24}H_{40}FeN_2Si_2$: C, 61.51; H, 8.60; Fe, 11.92; N, 5.98. Found: C, 61.33, 61.42; H, 8.43, 8.40; Fe, 11.53; N, 5.38, 5.26.

1,1′-Bis(dimethylchlorosilyl)ferrocene (IX) (*Crude*). A solution of 10.9 g. (0.023 mole) of 1,1′-bis[dimethyl(1-piperidyl)-silyl]ferrocene (VIII) in 450 ml. of anhydrous ether under nitrogen was stirred while hydrogen chloride was introduced into the solution for 30 min., 5 min. beyond the point at which the exit gas was acid to moist litmus. A white precipitate gradually formed. The mixture was stirred for an additional 2.5 hr., then filtered under nitrogen; the collected solid was washed with petroleum ether. The filtrate was evaporated under a stream of nitrogen below 10°, the residue was extracted with petroleum ether, and the extract was concentrated under nitrogen and refrigerated. The crystals which formed (6.4 g.) were collected and recrystallized from petroleum ether to give 5.3 g. (62%) of crude 1,1′-bis-(dimethylchlorosilyl)ferrocene (IX), m.p. 43–49°. After recrystallization, it melted at 44–49°.

Anal. Calcd. for $C_{14}H_{20}Cl_2FeSi_2$: Cl, 19.10; Fe, 15.04. Found: Cl, 17.19, 17.29, 17.29; Fe, 15.06.

A small sample of the crude material was also distilled at 0.03 mm. and then analyzed; m.p. 43–48°.

Anal. Found: Cl, 17.28; Fe, 15.42.

1,1′-Bis[3-(1′-phenyldimethylsilylferrocenyl)-1,1,3,3-tetramethyldisiloxanyl]ferrocene (X). The procedure for the preparation of VI was used with 11.7 g. (0.032 mole, *ca.*) of crude 1,1′-bis(dimethylchlorosilyl)ferrocene (IX) in place of 0.016 mole of tetrachlorosilane. From a fraction b.p. 90°/0.28 mm. to 85°/0.20 mm. was recovered 28% of the starting bridged ferrocene, I, m.p. 86–87.5°. When further distillation caused considerable smoking, the distillation residue was dissolved in petroleum ether and adsorbed on 500 g. of Woelm nonalkaline alumina, activity grade 1, in petroleum ether. Elution with 1500 ml. of petroleum ether-benzene (9:1) and 1600 ml. of petroleum ether–benzene (1:1) removed 16 g. of a reddish-brown oil. Distillation of this oil afforded 14.0 g. (41%) of crude X, b.p. 296–306°/0.09 mm., which was purified by redistillation; b.p. 310–320°/0.08 mm.

Anal. Calcd. for $C_{54}H_{70}Fe_3O_2Si_6$: C, 59.66; H, 6.49; Fe, 15.41. Found: C, 59.84, 59.99; H, 6.40, 6.43; Fe, 15.34.

Tris[(1′-phenyldimethylsilylferrocenyl)dimethylsiloxy]aluminum (XI) (*unsuccessful*). *1,3-Bis(1′-phenyldimethylsilylferrocenyl)-1,1,3,3-tetramethyldisiloxane* (XII). Aluminum chloride (2.8 g.; 0.021 mole) was used in place of methyltrichlorosilane in the method described above for the preparation of IV. By distillation was recovered 3.6 g. (18%) of the starting bridged ferrocene, I, m.p. 79–84°. The major distillation fraction, 10.5 g., b.p. 270–280°/0.15 mm., did not contain aluminum, and elemental analyses were in fair agreement with those calculated for 1,3-bis(1′-phenyldimethylsilylferrocenyl)tetramethyldisiloxane (XII) (43% conversion, or 53% yield based on recovered bridged ferrocene).

Anal. Calcd. for $C_{40}H_{50}FeOSi_4$: C, 62.33; H, 6.54; Fe, 14.49. Found: C, 61.91, 61.77; H, 6.56, 6.64; Fe, 14.12.

The infrared spectrum of this product was the same as that of 1,5-bis(1′-phenyldimethylsilylferrocenyl)hexamethyltrisiloxane (IV) except for a shoulder at 680 cm.$^{-1}$ and small intensity differences at 1100–1000 cm.$^{-1}$ and at 825–775 cm.$^{-1}$

Hydrolysis of lithium (1′-phenyldimethylsilyl-1-ferrocenyl)-dimethylsilanolate (II). *Phenyldimethylsilylferrocene* (XIII). An ether solution of II was prepared as described above, with the exception that the mole ratio of bromobenzene to the bridged compound was 3:1. The solution was cooled in an ice bath and 200 ml. of 10% aqueous ammonium chloride was added dropwise. The ether layer was then washed with water, dried over sodium sulfate, and evaporated *in vacuo*. Distillation of the residue gave 3 g. of pale-yellow liquid, b.p. 50–51°/0.17 mm., 16.0 g. of solid, b.p. 150–165°/0.2 mm., and 6.6 g. of liquid collected at a pot temperature of 280° under 0.03 mm. pressure. By recrystallization of the middle fraction from methanol, 12 g. (60%) of phenyldimethylsilylferrocene (XIII), m.p. 80–83°, was isolated. It was recrystallized twice from methanol, and then fractionally sublimed (m.p. 83–84.5°).

Anal. Calcd. for $C_{18}H_{19}FeSi$: C, 67.50; H, 6.29; Fe, 17.44. Found: C, 67.59, 67.66; H, 6.12, 6.04; Fe, 17.19, 17.52.

The infrared spectrum of the final fraction (6.6 g.) was identical with that of 1,5-bis(1′-phenyldimethylsilyl-1-ferrocenyl)hexamethyltrisiloxane (IV), but the elemental analyses were far from the calculated values for this trisiloxane. This product, XV, may have been a mixture of the corresponding tetrasiloxane, $C_{44}H_{62}Fe_2O_3Si_6$, and the pentasiloxane, $C_{46}H_{68}Fe_2O_4Si_7$, both of which would be expected to have spectra very similar to the trisiloxane.

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[21] G. Wilkinson, *Org. Syntheses*, **36**, 31 (1956).

Anal. Calcd. for $C_{44}H_{62}Fe_2O_3Si_6$: C, 57.48; H, 6.80; Fe, 12.15. Calcd. for $C_{46}H_{68}Fe_2O_4Si_7$: C, 55.62; H, 6.90; Fe, 11.24. Found: C, 56.12; H, 6.77; Fe, 11.80, 11.84.

1-Trimethylsilyl-1′-(3-phenyl-1,1,3,3-tetramethyldisiloxanyl)ferrocene (XVII). Methyllithium was prepared by the addition of 13.8 g. (0.095 mole) of methyl iodide in 30 ml. of ether during a 35-min. period to 1.6 g. of lithium slices in 100 ml. of ether cooled in an ice bath. The mixture was stirred 1 hr. at room temperature and then refluxed for 1 hr. This solution was added to 20 g. (0.063 mole) of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (I) in 250 ml. of ether and the mixture refluxed for 4 days. Phenyldimethylchlorosilane (10.7 g.; 0.063 mole) in 50 ml. of ether was then added and the mixture stirred at room temperature overnight and filtered. The filtrate was washed with water, the ether layer dried over sodium sulfate, and ether removed *in vacuo.* Distillation of the residue gave 15.3 g. (52%) of XVII, b.p. 148–151°/0.09 mm. No starting I was recovered.

Anal. Calcd. for $C_{23}H_{34}FeOSi_3$: Fe, 11.97. Found: Fe, 12.41.

In an earlier run, the cleavage reaction was performed in benzene at 75° overnight, and water was not used in the workup. From material soluble in petroleum ether was isolated 24% of the starting bridged ferrocene, I, and 22% of the desired XVII, b.p. 140–144°/0.03 mm., after two distillations. The infrared spectra of the compound from the two preparations were identical.

Anal. Calcd. for $C_{23}H_{34}FeOSi_3$: C, 59.20; H, 7.34; Fe, 11.97. Found: C, 59.15, 59.14; H, 7.42, 7.40; Fe, 11.99, 12.18.

1,5-Bis(1′-trimethylsilylferrocenyl)-1,1,3,3,5,5-hexamethylsiloxane (XVIII). The above procedure for the cleavage of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (I) in ether with methyllithium was repeated, except that the resulting solution was refluxed 3 days instead of 4. The mixture was then treated with 4.1 g. (0.0318 mole) of dimethyldichlorosilane in 40 ml. of ether, added in one portion. After the mixture had stirred overnight, it was filtered, the filtrate washed with water and then dried and evaporated *in vacuo.* Distillation of the residue furnished two main fractions: 10.0 g., b.p. 90–115°/0.14 mm., and 8.5 g., b.p. 210–218°/0.09 mm. The second fraction was XVIII (37%).

Anal. Calcd. for $C_{32}H_{52}Fe_2O_2Si_5$: C, 53.31; H, 7.27; Fe, 15.49. Found: C, 53.78, 53.57; H, 7.31, 7.24; Fe, 15.94.

Filtration of the first fraction and recrystallization of the solid gave 0.5 g. (2.5%) of the starting bridged ferrocene, I.

1-Ferrocenyl-3-phenyl-1,1,3,3-tetramethyldisiloxane (XX). Sodamide was prepared by addition of 6.9 g. (0.30 mole) of sodium and a crystal of ferric nitrate to 200 ml. of liquid ammonia. The mixture was stirred while partially submerged in a −70° bath and 20.0 g. (0.063 mole) of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (I) was added in several portions. After the mixture was stirred 4 hr., the bath was removed, and the mixture stirred an additional 2 hr. After the ammonia had evaporated, the residue was extracted with ether, the extract evaporated to dryness, and the residue again taken up in ether and evaporated, in order to assure complete absence of ammonia. The residue was then dissolved in 150 ml. of ether and treated dropwise with a solution of 10.8 g. (0.063 mole) of phenyldimethylchlorosilane in 75 ml. of ether. After 3 hr., the mixture was filtered, the solid washed with ether, and the filtrate evaporated under vacuum. The residue was dissolved in 100 ml. of dioxane, 0.57 g. (0.0316 mole) of water was added, and the solution was refluxed for 75 min. Removal of solvent and distillation of the residue gave 4.1 g. of a forerun, not highly colored, and 12.2 g. (49%) of orange-brown 1-ferrocenyl-3-phenyltetramethyldisiloxane (XX), b.p. 142–152°/0.2 mm. The crude XX was redistilled, b.p. 144.5–148°/0.1 mm., n_D^{25} 1.5569.

Anal. Calcd. for $C_{20}H_{26}FeOSi_2$: C, 60.90; H, 6.64; Fe, 14.16. Found: C, 60.20, 60.18; H, 6.82, 6.95; Fe, 14.02.

The infrared spectrum of the product showed bands in the siloxane region.

In initial experiments the bridged ferrocene (I) did not react with sodamide in refluxing benzene during a 20-hr. period, and reaction with sodamide in liquid ammonia was incomplete at the end of 1 hr.

1-Dimethyl(1-piperidyl)silyl-1′-(3-phenyltetramethyldisiloxanyl)ferrocene (XXI). A solution of *n*-butyllithium, prepared[22] from 0.056 mole of *n*-butyl bromide, was added during a 10-min. period to 4.25 g. (0.05 mole) of piperidine in 50 ml. of ether. After the solution was stirred for 1.5 hr., 15.8 g. (0.05 mole) of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (I) was added and the mixture stirred 20 hr. Phenyldimethylchlorosilane (8.6 g.; 0.05 mole) in 10 ml. of ether was then introduced and stirring continued for 4 hr. The reaction mixture was evaporated to dryness *in vacuo,* the residue was extracted with petroleum ether, and the extract distilled. From a fraction, b.p. 90–100°/0.4 mm., 4.8 g. (30%) of the starting bridged ferrocene (I), m.p. 86–87.5°, was recovered by recrystallization from isopropyl alcohol. A high-boiling fraction, 12.7 g. (47%), b.p. 204–210°/0.35 mm., n_D^{25} 1.5509 was the desired XXI.

Anal. Calcd. for $C_{27}H_{41}FeNOSi_3$: C, 60.54; H, 7.71; Fe, 10.43; N, 2.26. Found: C, 60.67; 60.80; H, 7.85, 7.82; Fe, 10.55, 10.38; N, 2.23, 2.21.

When the cleavage mixture was refluxed for 4 hr. instead of stirred at room temperature overnight, the yield of XXI was 49% (72% based on recovered I).

1,3-Bis[1′-(3-phenyltetramethyldisiloxanyl)ferrocenyl]-tetramethyldisiloxane (XXIII). To 8.69 g. (0.0162 mole) of 1-dimethyl(1-piperidyl)silyl-1′-(3-phenyltetramethyldisiloxanyl)ferrocene (XXI) in 8 ml. of dioxane was added 0.146 g. (0.0081 mole) of water in 0.85 g. of dioxane. The mixture was allowed to stand 1 hr. and then refluxed for 1 hr. Removal of solvent by evaporation *in vacuo* and distillation of the residue gave 6.0 g. (81%) of the desired XXIII, b.p. 290–300°/0.3 mm. This procedure was then repeated with doubled quantities, and the product XXIII, 12.1 g. (82%), b.p. 283–298°/0.09 mm., combined with the first lot and redistilled; b.p. 283–290°/0.025 mm., n_D^{25} 1.5572.

Anal. Calcd. for $C_{44}H_{62}Fe_2O_2Si_6$: C, 57.49; H, 6.80; Fe, 12.15. Found: C, 57.43, 57.31; H, 6.95; 6.85; Fe, 12.07.

WYANDOTTE, MICH.

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[22] R. G. Jones and H. Gilman, *Organic Reactions,* 6, 339 (1951).