chloride, and the extracts were added to the ethylene chloride layer. The combined chlorocarbon layers were washed with water until neutral, and dried over Drierite. The solvents were removed to leave a red, mobile oil which very slowly crystallized. This crystalline solid was collected and recrystallized twice from hexane to give 7.0 g. (41%) of ketone VII, m.p. 85.5–86°, as small orange-red needles. Further recrystallizations did not raise the melting point. Mixed melting points and infrared spectra showed that this compound was identical with that obtained from the hydrogenation of the benzal derivative II.

*Monophenylhydrazone of yellow product.* To a solution of 1 g. of the yellow product in 250 ml. of boiling absolute ethanol was added 4 g. of phenylhydrazine. This solution was heated on the steam bath for 30 min., and then 3.5 ml. of concd. hydrochloric acid was added. The solution was cooled in the refrigerator overnight to precipitate a brown powder. Recrystallization from absolute ethanol gave 0.3 g. (25%) of tan needles, m.p. 200–201°, the analysis of which was satisfactory for a monophenylhydrazone of a monobenzaldehyde derivative of bisacetylferrocene.

*Anal.* Calcd. for $C_{27}H_{24}N_2OFe$: C, 72.10; H, 5.35; N, 6.24; Fe, 12.4. Found: C, 72.22; H, 4.96; N, 6.12; Fe, 12.02.

*Mono-2,4-dinitrophenylhydrazone of yellow product.* To a solution of 1 g. of the yellow product in 100 ml. of absolute ethanol was added 2 g. of 2,4-dinitrophenylhydrazine in 25 ml. of absolute ethanol. This solution was heated on the steam bath for 10 min., and then 3 ml. of concd. hydrochloric acid was added. The solution was cooled in the refrigerator to precipitate 1 g. (66%) of purple needles, m.p. >300°, the analysis of which was satisfactory for a mono-2,4-dinitrophenylhydrazone of a monobenzaldehyde derivative of bisacetylferrocene.

*Anal.* Calcd. for $C_{27}H_{22}N_4O_5Fe$: C, 60.24; H, 4.12; N, 10.41; Fe, 10.37. Found: C, 59.98; H, 3.84; N, 10.08; Fe, 10.27.

DURHAM, N. C.

---

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

# Ferrocenes. I. Synthesis of Siloxanylferrocenes[1,2]

ROBERT L. SCHAAF, PETER T. KAN, CARL T. LENK, AND EVA P. DECK

*Received April 11, 1960*

The reaction of cyclopentadienyllithium with dimethyldichlorosilane, 1,3-dichlorotetramethyldisiloxane, and 1,5-dichlorohexamethyltrisiloxane gave monochloro derivatives which furnished unsymmetrical cyclopentadienylsiloxanes upon treatment either with a sodium silanolate or with water and a chlorosilane. From the cyclopentadienylsiloxanes, a series of siloxanylferrocenes was prepared by treatment with butyllithium and ferrous chloride. Similarly, 1,1′-bis(3-phenyltetramethyldisiloxanyl)-*x*,*x*′-dimethylferrocene and 1,1′-bis(chloromethyldimethylsilyl)ferrocene were synthesized. From the latter, 1,1′-bis(aminomethyldimethylsilyl)ferrocene dihydrochloride was prepared.

Silicon-substituted ferrocenes previously described have been mono- or bis(triarylsilyl)ferrocenes or trialkylsilylferrocenes and were prepared either by addition of a trisubstituted chlorosilane to metalated ferrocene[3–5] or by treatment of a trisubstituted-silyl cyclopentadiene successively with butyllithium and ferrous chloride.[5] By application of the latter method to cyclopentadienylsiloxanes we have prepared a series of siloxanylferrocenes. A major part of this paper describes the synthesis of the precursor cyclopentadienylsiloxanes, which, like the siloxanylferrocenes, are a class of compound not previously described in literature.

A compound desired for the synthesis of cyclopentadienylsiloxanes was cyclopentadienyldimethylchlorosilane (Ia). The reaction of cyclopentadienylmagnesium bromide with dimethyldichlorosilane in benzene has been described, but despite a 75% excess of dimethyldichlorosilane, the main product, obtained in about 40% yield, was bis(cyclopentadienyl)dimethylsilane[6] and not Ia. A by-product, obtained in 11% yield and which was not specifically named or characterized, was called cyclopentadienyldimethylchlorosilane in a related patent,[7] but the reported boiling point, 80–83°/0.7 mm., is too high for the monomer. Cyclopentadienyltrichlorosilane, b.p. 50–55°/10 mm., has been described, prepared in 56% yield from cyclopentadienylsodium and a five- to seven-fold excess of silicon tetrachloride in xylene.[8]

When cyclopentadienyllithium was treated with two moles of dimethyldichlorosilane in ether, cyclopentadienyldimethylchlorosilane[9] (Ia) was obtained in 69% yield. Regarding the mode of addition, it would be logical to add the cyclopentadienyllithium to the dimethyldichlorosilane, but the order of addition was not important to good yield or

---

(1) Presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959.

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

(3) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954); R. A. Benkeser, U. S. Patent 2,831,880 (Apr. 22, 1958).

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

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

(6) K. C. Frisch, *J. Am. Chem. Soc.*, 75, 6050 (1953).

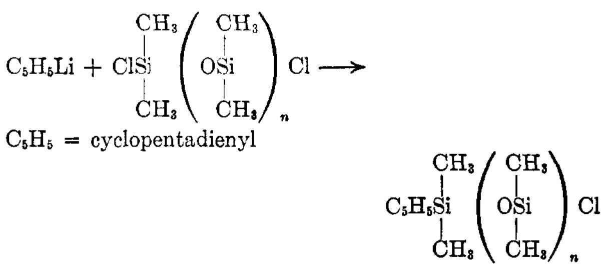
(7) R. W. Martin, U. S. Patent 2,667,501 (Jan. 26, 1954).

(8) Enjay Company, Inc., *High Purity Dicyclopentadiene, Technical Bulletin No. 12*, 18.

(9) Throughout this paper compounds containing a monosubstituted cyclpentadiene ring are referred to without designation of the relative position of the substituent and double bonds in the ring. The position of attachment is not important to the investigation, inasmuch as the final products prepared from the cyclopentadiene compounds are ferrocenes, in which the ring positions are equivalent.

purity. When methyltrichlorosilane was used, cyclopentadienylmethyldichlorosilane (II) was obtained in 55% yield. The preparation of II from cyclopentadienylmagnesium bromide was claimed in a patent,[7] but physical data were not given, and the reported boiling point (137–140°/0.7 mm.) of the diacetoxy derivative by which the compound was identified seems to be too high for the monomer. Methylcyclopentadienyllithium with dimethyldichlorosilane furnished methylcyclopentadienyldimethylchlorosilane (III) in 71% yield.

When 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane were employed in place of dimethyldichlorosilane, cyclopentadienyllithium reacted to give the desired cyclopentadienylchlorosiloxanes, Ib and Ic, respectively.

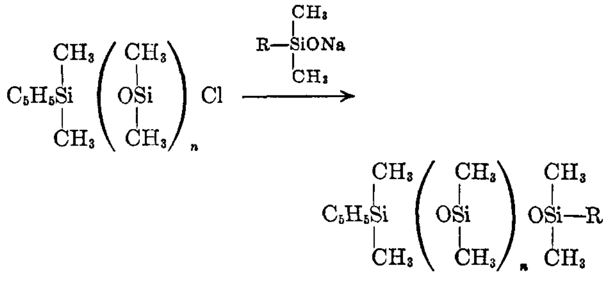


$$C_5H_5Li + Cl\underset{CH_3}{\overset{CH_3}{Si}}\left(O\underset{CH_3}{\overset{CH_3}{Si}}\right)_n Cl \longrightarrow C_5H_5\underset{CH_3}{\overset{CH_3}{Si}}\left(O\underset{CH_3}{\overset{CH_3}{Si}}\right)_n Cl$$

$C_5H_5$ = cyclopentadienyl

Ia. $n = 0$
Ib. $n = 1$
Ic. $n = 2$

Of the general methods available for the preparation of unsymmetrical siloxanes from halosilanes,[10] the reaction with metal silanolates[11] is the most straightforward. Treatment of compounds Ia-Ic and III with sodium phenyldimethylsilanolate in ether gave 61–80% yields of the desired siloxanes, IVa-IVc, and 1-(methylcyclopentadienyl)-3-phenyltetramethyldisiloxane (V), respectively. Similarly, cyclopentadienylpentamethyldisiloxane (IVd) was formed from Ia and sodium trimethylsilanolate.



$$C_5H_5\underset{CH_3}{\overset{CH_3}{Si}}\left(O\underset{CH_3}{\overset{CH_3}{Si}}\right)_n Cl \xrightarrow{R-\underset{CH_3}{\overset{CH_3}{Si}}ONa} C_5H_5\underset{CH_3}{\overset{CH_3}{Si}}\left(O\underset{CH_3}{\overset{CH_3}{Si}}\right)_n O\underset{CH_3}{\overset{CH_3}{Si}}-R$$

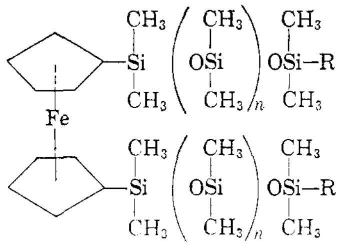
$C_5H_5$ = cyclopentadienyl

IVa. R = $C_6H_5$, $n = 0$
IVb. R = $C_6H_5$, $n = 1$
IVc. R = $C_6H_5$, $n = 2$
IVd. R = $CH_3$, $n = 0$

Another method for the preparation of cyclopentadienylsiloxanes was based upon the *in situ* formation of cyclopentadienyldimethylsilanol from Ia. After Ia in cold dioxane-ether had been treated with two moles of pyridine and one mole of water in order to form the silanol, the subsequent addition of one mole of trimethylchlorosilane furnished pure cyclopentadienylpentamethyldisiloxane (IVd) in 53% yield. By this method (Method B) three cyclopentadienyldisiloxanes, IVa, IVd, and 1-cyclopentadienyl - 3 - (dichlorophenyl)tetramethyldisiloxane (IVe), were prepared in 46–66% yields.

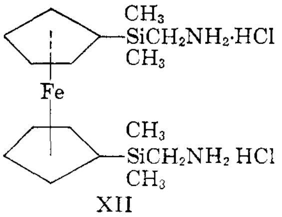
Triphenylsilanol reacted slowly with Ia in ether in the presence of pyridine to give 1-cyclopentadienyl-1,1-dimethyl-3,3,3-triphenyldisiloxane (VI) in 57% yield.

From the above cyclopentadienylsiloxanes (IVa-IVe, V, and VI), the corresponding siloxanylferrocenes VIIa-VIIe, 1,1′-bis(3-phenyltetramethyldisiloxanyl)-x,x′-dimethylferrocene (VIII), and 1,1′-bis(3,3,3 - triphenyl - 1,1 - dimethyldisiloxanyl)ferrocene (IX) were prepared by conversion to the lithio derivative with butyllithium in ether followed by treatment of the lithio derivative in tetrahydrofuran with ferrous chloride. With these reagents Goldberg, *et al.*, prepared 1,1′-bis(trimethylsilyl)ferrocene in 50% yield from trimethylsilylcyclopentadiene.[5] Yields of siloxanylferrocenes were 36–59%.



VIIa. R = $C_6H_5$, $n = 0$
VIIb. R = $C_6H_5$, $n = 1$
VIIc. R = $C_6H_5$, $n = 2$
VIId. R = $CH_3$, $n = 0$
VIIe. R = $C_6H_3Cl_2$, $n = 0$
$C_6H_3Cl_2$ = *x,x*-dichlorophenyl

The conversion to ferrocenes was also successful when the substituent on the cyclopentadienyl ring contained a chloromethyl group. With butyllithium and ferrous chloride, crude cyclopentadienylchloromethyldimethylsilane, obtained in 72% yield from chloromethyldimethylchlorosilane, was converted to 1,1′-bis(chloromethyldimethylsilyl)ferrocene (X) in 39% yield. Compound X in very crude form (86% yield) could be converted to the corresponding diamine dihydrochloride (XII) in 45% yield *via* the bis(phthalimide) (XI).[12]



XII

---

(10) General methods have been described or referred to by W. H. Daudt and J. F. Hyde, *J. Am. Chem. Soc.*, **74**, 386 (1952).

(11) 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).

(12) S. Gabriel, *Ber.*, **20**, 2224 (1887); H. R. Ing and R. H. F. Manski, *J. Chem. Soc.*, 2348 (1926).

TABLE I

CYCLOPENTADIENYLCHLOROSILANES AND CYCLOPENTADIENYLCHLOROSILOXANES

| Compound | Formula | Yield, % | B.P./mm.[a] | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Chlorine, % Calcd. | Chlorine, % Found | Silicon, % Calcd. | Silicon, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | $C_7H_{11}ClSi$ | 69 | 37–40/7–4.5 | 52.97 | 53.08 | 6.99 | 6.87 | 22.34 | 22.36 | 17.70 | 17.81 |
| Ib | $C_9H_{17}ClOSi_2$ | 57 | 62–82/3–4 | 46.42 | 46.19 | 7.36 | 7.68 | 15.23 | 15.4 | 24.12 | 24.41 |
| Ic | $C_{11}H_{23}ClO_2Si_3$ | 40[b] | 62–100/1.5–2 | 43.03 | 43.44 | 7.55 | 7.28 | 11.55 | 11.53 | 27.45 | 26.71 |
| II | $C_8H_8Cl_2Si$ | 55 | 36–50/3.5 | 40.23 | 39.81 | 4.50 | 4.81 | 39.59 | 39.09 | 15.68 | 15.66 |
| III | $C_8H_{13}ClSi$ | 71 | 75–90/20 | 55.63 | 55.35 | 7.59 | 7.93 | 20.53 | 20.42 | 16.25 | 16.11 |

[a] The wide boiling ranges but satisfactory analyses suggest some dimer may be present. [b] In subsequent runs, the yield varied from 9–26%.

TABLE II

CYCLOPENTADIENYLSILOXANES

| Compound | Formula | Method[a] | Yield, % | B.P./mm. | $n_D^{25}$ | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Silicon, % Calcd. | Silicon, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IVa | $C_{15}H_{22}OSi_2$ | A | 80 | 83–86/0.03–0.05 | 1.5004 | 65.63 | 65.81 | 8.08 | 8.07 | 20.46 | 20.33 |
| | | B | 66 | 81–89/0.2 | 1.4987 | | | | | | |
| IVb | $C_{17}H_{28}O_2Si_3$ | A | 76 | 107–112/0.04–0.07 | 1.4797 | 58.56 | 58.39 | 8.09 | 8.09 | 24.17 | 24.53 |
| IVc | $C_{19}H_{34}O_3Si_4$ | A | 61 | 116–144/0.09 | 1.4653 | 53.97 | 53.53 | 8.11 | 8.09 | 26.57 | 26.64 |
| IVd | $C_{10}H_{20}OSi_2$ | A | 66 | 82–83/21 | 1.4391 | 56.53 | 56.83 | 9.49 | 9.76 | 26.45 | 26.05 |
| | | B | 53 | 78–81/20 | 1.4390 | 56.53 | 56.37 | 9.49 | 9.39 | | |
| IVe | $C_{15}H_{20}Cl_2OSi_2$ | B | 46 | 102/0.03 | 1.5245 | 52.46 | 52.42 | 5.87 | 5.64 | 16.36<br>20.65[b] | 16.43<br>20.63[b] |
| V | $C_{16}H_{24}OSi_2$ | A | 79 | 82–85/0.16 | 1.4968 | 66.60 | 66.24 | 8.38 | 8.96 | 19.47 | 19 27 |
| VI | $C_{25}H_{26}OSi_2$ | [a] | 57 | 156–159/0.05 | 1.5788 | 75.32 | 74.94 | 6.57 | 6.79 | 14.09 | 13.96 |

[a] See Experimental. [b] Chlorine, %.

## EXPERIMENTAL[13]

*Cyclopentadienylchlorosilanes and cyclopentadienylchlorosiloxanes* (Table I). The following procedure for the preparation of 1-cyclopentadienyl-3-chlorotetramethyldisiloxane (Ib) is representative of the procedures employed for the preparation of the compounds listed in Table I. A solution of *n*-butyllithium prepared[14] from 0.9 mole of *n*-butyl bromide was added dropwise during a 1-hr. period to a stirred solution of 59.5 g. (0.9 mole) of cyclopentadiene in 500 ml. of anhydrous ether under nitrogen in an ice bath. After the mixture was stirred an additional 1.5 hr. without the bath, a mixture of 365 g. (1.8 moles) of 1,3-dichlorotetramethyldisiloxane[15] in 350 ml. of ether was added in one portion and the mixture refluxed overnight. The volume of the mixture was reduced by vacuum distillation, the mixture filtered through a fritted glass filter, and the solid washed with ether. After removal of volatile material from the filtrate under vacuum, distillation of the residue through a 20-cm. Vigreux column gave a fraction, 203 g., b.p. 46°/14 mm.–75°/6 mm., and a second fraction, 95.1 g., b.p. 71–100°/4 mm. By redistillation of the first fraction, 197 g. (54%) of 1,3-dichlorotetramethyldisiloxane, b.p. 42–46°/22 mm., was recovered. The second fraction, redistilled for analysis, furnished 76.4 g. (36%) of Ib, b.p. 62–82°/3–4 mm. In a repeat run, the yield of material b.p. 53°/1.5 mm. to 60°/0.7 mm. was 57%.

When tetrahydrofuran was substituted for ether in the above procedure and the mode of addition was cyclopentadienyllithium to dichlorosiloxane, compound Ib, b.p. 51–71°/1.5 mm., was obtained in 15% yield. The temperature of the refluxing reaction mixture was 55°.

Cyclopentadienyldimethylchlorosilane (Ia) was prepared as described for Ib and by variations of the method as shown in Table IV.

For conversion of cyclopentadienyllithium to Ic, the reaction time was doubled (40 hr.) and the product, obtained in 40% yield, was not redistilled before analysis. A repeat run gave a 25% yield of Ic, b.p. 72–86°/1.2 mm. When the reaction time was 20 hr., yields of 19, 26, and 9% were obtained.

For the isolation of II, the following procedure was used. After the mixture had refluxed overnight, the precipitate was allowed to settle, the clear layer was forced with nitrogen into distillation equipment, and the solid was washed with petroleum ether and finally filtered. Removal of solvent from the decanted solution and washes and distillation of the residue through a 30-cm. Vigreux column furnished II (55%), b.p. 35–42°/3.5 mm. In an initial run, the product (41%), b.p. 36–50°/3.5 mm., was subjected to elemental analysis (Table I).

*Cyclopentadienylsiloxanes from sodium silanolates* (Table II, Method A). Cyclopentadienylpentamethyldisiloxane (IVd) and the cyclopentadienylphenylsiloxanes IVa–IVc and V were prepared by similar procedures from the required chlorosilanes and sodium silanolates (sodium trimethylsilanolate[11] and sodium phenyldimethylsilanolate[11]). The following procedure for the preparation of 1-cyclopentadienyl-3-phenyltetramethyldisiloxane (IVa) is typical. Cyclopentadienyldimethylchlorosilane (Ia) (39.7 g.; 0.25 mole) in 100 ml. of anhydrous ether was stirred under nitro-

---

(13) All melting points and boiling points were uncorrected. Analyses of ferrocenes were by the Schwartzkopf Microanalytical Laboratory, Woodside 77, New York. Other analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich. Distillations were in general performed under nitrogen, and products were stored under nitrogen in amber bottles. Heating of mixtures containing cyclopentadiene compounds was kept to a practical minimum during isolations, in an effort to avoid dimerization.

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

(15) British Thomson-Houston Co., Ltd., Brit. Patent 631,018 (Oct. 25, 1949).

TABLE III

SILOXANYLFERROCENES

| Compound | Formula | Yield, % | B.P./Mm. | $n_D^{25}$ | $d_4^{25}$ | Carbon, % |  | Hydrogen, % |  | Iron, % |  | Silicon, % |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| VIIa | $C_{30}H_{42}FeO_2Si_4$ | 59 | 200–205/0.03[a] | 1.5473 | 1.1063 | 59.76 | 59.94 | 7.02 | 6.93 | 9.26 | 9.36[c] |  |  |
| VIIb | $C_{34}H_{54}FeO_4Si_6$ | 50 | 220–223/0.15 | 1.5162 | 1.0796 | 54.36 | 54.35 | 7.25 | 7.34 | 7.43 | 7.59 | 22.44 | 22.02 |
| VIIc | $C_{38}H_{66}FeO_6Si_8$ | 36 | 245–255/0.04 | 1.4850 |  | 50.74 | 50.72 | 7.40 | 7.51 | 6.21 | 5.95 | 24.98 | 25.11 |
| VIId | $C_{20}H_{38}FeO_2Si_4$ | 55 | 107–110/0.01 | 1.4940 | 1.0308 | 50.18 | 50.19 | 8.00 | 8.18 | 11.66 | 11.60 | 23.47 | 23.44 |
| VIIe | $C_{30}H_{38}Cl_4FeO_2Si_4$ | 47 | 263–265/0.12 | 1.5675 | 1.2591 | 48.65 | 48.87 | 5.17 | 5.20 | 7.54 | 7.48 | 15.17<br>19.15[d] | 15.05<br>19.15[d] |
| VIII | $C_{32}H_{46}FeO_2Si_4$ | 52 | 205–215/0.07 | 1.5428 | 1.0863 | 60.92 | 61.40 | 7.35 | 7.42 | 8.85 | 8.6 | 17.81 | 17.8 |
| IX | $C_{50}H_{50}FeO_2Si_4$ | 37 | [b] |  |  | 70.56 | 70.43 | 5.92 | 5.70 | 6.56 | 6.50 |  |  |

[a] M.p. 18–19.5°. [b] M.p. 148.5–150°. [c] On material m.p. 19.5–20°. [d] Chlorine, %.

TABLE IV

PREPARATION OF CYCLOPENTADIENYLDIMETHYLCHLOROSILANE (Ia)

| Reactant Ratio[a] | Mode of Addition | Yield, % | B.P./Mm. | Hydrolyzable Chlorine, %[b] |
|---|---|---|---|---|
| 1:5 | Indirect[c] | 58 | 62–69/22 |  |
| 1:5 | Direct | 57 | 63–75/24 | 21.5 |
| 1:2 | Indirect | 53 | 62–74/24[d] | 22.0 |
| 1:2 | Direct | 60 | 63–75/24[d] | 20.4 |
| 1:2 | Direct | 67 | 31–38/5 | 22.3 |
| 1:2 | Direct | 69 | 37–40/7–4.5 | 22.4 |

[a] Ratio of cyclopentadiene to dimethyldichlorosilane. [b] Calcd. for $C_7H_{11}ClSi$: 22.34%. [c] Cyclopentadienyllithium to dimethyldichlorosilane. [d] Continued distillation up to 20° above this range gave a fraction which upon redistillation furnished additional product (7–18%) boiling within this range; the stated yield includes this material, which contained 20–21.6% hydrolyzable chlorine.

gen in an ice bath while a solution of 43.5 g. (0.25 mole) of sodium phenyldimethylsilanolate in 100 ml. of anhydrous ether was added during a 5-min. period. The mixture was allowed to come to room temperature while it was stirred overnight. Precipitated solid was removed by centrifugation and washed with ether, and the combined filtrate and washes were evaporated *in vacuo*. Distillation of the residue gave 55.0 g. (80%) of compound IVa.

The tetrasiloxane IVc, b.p. 124–144°/0.06 mm., was obtained in 61% yield after two distillations, and was distilled again before it was analyzed.

Compound IVd, prepared in 66% yield, b.p. 76–81°/21 mm., was redistilled through a 25-cm. column for analysis.

*Cyclopentadienylsiloxanes from chlorosilanes* (Table II, Method B). The procedure given below for the preparation of cyclopentadienylpentamethyldisiloxane (IVd) is representative for those compounds in Table II prepared by Method B. Trimethylchlorosilane, phenyldimethylchlorosilane,[16] and *x,x*-dichlorophenyldimethylchlorosilane[16] were freshly distilled. A solution of 15.9 g. (0.1 mole) of cyclopentadienyldimethylchlorosilane (Ia) in a mixture of 50 ml. of anhydrous ether and 50 ml. of anhydrous dioxane was stirred under nitrogen in an ice bath while 15.8 g. (0.2 mole) of pyridine was added during a 5-min. period. After 10 min., 1.8 ml. (0.1 mole) of water in a mixture of 25 ml. of ether and 25 ml. of dioxane was added in one portion and followed 45 min. later by 10.7 g. (0.1 mole) of trimethylchlorosilane in 25 ml. of ether, added in a slow stream. The mixture was stirred overnight and the precipitated solid was removed by filtration and washed with ether. The filtrate was evaporated *in vacuo* and the residue distilled; there was less than 1 ml. of liquid remaining after the main fraction (15.8 g.), b.p. 60–84°/20 mm., $n_D^{25}$ 1.4386, was collected. Redistillation of the main fraction gave 11.2 g. (53%) of IVd.

For the preparation of the 3-phenyl compound (IVa) hydrolyzable chlorine analyses of Ia and phenyldimethylchlorosilane were made, and the amounts of each chlorosilane employed were such that the quantities of hydrolyzable chlorine in each amount were equal. This was also true in the case of the 3-(*x,x*-dichlorophenyl) compound (IVe); in this instance a center cut from the second distillation of the product, b.p. 100–103°/0.03 mm., was taken for elemental analysis.

*1-Cyclopentadienyl-1,1-dimethyl-3,3,3-triphenyldisiloxane* (VI). Cyclopentadienyldimethylchlorosilane (Ia) (52.9 g.; 0.333 mole) in 400 ml. of ether was cooled in an ice bath under nitrogen, and treated with 26.4 g. (0.333 mole) of pyridine. Triphenylsilanol (97.5 g., 0.353 mole) was then

---

[16] Technical grade; Dow Corning Corporation, Midland, Mich.

washed into the mixture with 100 ml. of ether, and the reaction mixture was refluxed overnight. Solids were removed by filtration and were washed with petroleum ether (b.p. 30–60°) and with ether. The filtrate and washes were combined and evaporated *in vacuo*, the residue was extracted with 200 ml. of petroleum ether, and the insoluble, unchanged triphenylsilanol (29 g.) was removed by filtration and washed with 100 ml. of petroleum ether. By distillation of the combined extract and washes, 83.4 g. of liquid, b.p. 160°/0.13 mm. to 165°/0.07 mm., was obtained. Redistillation furnished VI, Table II.

*Siloxanylferrocenes* (Table III). The method for the preparation of the ferrocenes listed in Table III is illustrated by the synthesis of 1,1′-bis[3-(*x*,*x*-dichlorophenyl)tetramethyldisiloxanyl]ferrocene (VIIe). *n*-Butyllithium solution, prepared[14] from 0.175 mole of *n*-butyl bromide, was added during a 1.5-hr. period to a solution of 60 g. (0.175 mole) of 1-cyclopentadienyl-3-(*x*,*x*-dichlorophenyl)tetramethyldisiloxane (IVe) in 175 ml. of anhydrous ether with stirring under a blanket of nitrogen. The mixture was stirred and refluxed overnight and then cooled. Ferrous chloride solution, which had been freshly prepared[17] from 9.5 g. (0.0585 mole) of ferric chloride and 1.65 g. of 325-mesh reduced iron, was washed into the stirred mixture with 175 ml. of anhydrous tetrahydrofuran. Solvent was removed by distillation until the boiling point of the distillate was 55°, and the mixture was stirred and refluxed overnight under nitrogen. The reaction mixture was then evaporated *in vacuo* and the residue extracted with petroleum ether. Removal of solvent from the extract and fractionation of the residue gave 30.9 g. (47%) of VIIe, b.p. 263–265°/0.12 mm.

Compound VIIa prepared in this manner melted at 18–19.5°; a sample, m.p. 19.5–20°, $n_D^{25}$ 1.5474, was obtained by distillation through a 60-cm. column packed with glass helices.

In the preparation of VIIb, VIId, and IX the ferrous chloride solution was added 2 to 3 hr. after completion of the addition of *n*-butyllithium solution. For analysis of VIId, the first of two distillation fractions was taken: fraction 1 (41%), b.p. 107–109°/0.01 mm., and fraction 2 (14%), b.p. 106–110°/0.03–0.07 mm.

The reaction of *n*-butyllithium with VI was conducted in an ice bath. For subsequent isolation of IX, the final reaction mixture was evaporated to dryness under vacuum, the residue was extracted with boiling heptane, and the extracts were taken to dryness. By crystallization of the residue from hexane, the desired IX (37%), m.p. 146–149°, was obtained. It was recrystallized from acetone for analysis (Table III).

*1,1′-Bis(chloromethyldimethylsilyl)ferrocene* (X). Cyclopentadienyllithium in ether (1200 ml.) was prepared in the usual manner from 66.1 g. (1 mole) of cyclopentadiene and *n*-butyllithium, prepared[14] from 1 mole of *n*-butyl bromide. To the solution of cyclopentadienyllithium was added in one portion 143 g. (1 mole) of chloromethyldimethylchlorosilane[18] in 200 ml. of ether under nitrogen. The mixture was refluxed overnight, filtered, and the fitrate stripped of solvent *in vacuo*. The residual liquid was distilled through a 15-cm. Vigreux column to give 125 g. (72%) of crude cyclopentadienylchloromethyldimethylsilane, b.p. 48–52°/1.5 mm.

A solution of *n*-butyllithium prepared from 0.78 mole of *n*-butyl bromide was added dropwise during a 30-min. period to a stirred solution of 121 g. (0.70 mole) of this crude material in 350 ml. of tetrahydrofuran, kept at −20 to −30° under nitrogen. The mixture was stirred for an additional 45 min. at −30°. A slurry of ferrous chloride and tetrahydrofuran, freshly prepared[17] from 39.3 g. (0.243 mole) of ferric chloride and 7.2 g. of iron powder in 150 ml. of tetrahydrofuran, was cooled to −30° and added in one portion to the above mixture. The mixture was stirred overnight as it was allowed to warm to room temperature, and volatile materials were then removed *in vacuo*. The residue was mixed with petroleum ether until solids formed, the insoluble solids were filtered and washed thoroughly with petroleum ether, and the filtrate was evaporated *in vacuo*. The residue was then dissolved in 100 ml. of petroleum ether, refrigerated overnight, and filtered. Volatile material was removed from the filtrate under vacuum, and unchanged cyclopentadienylchloromethyldimethylsilane was removed by evaporation at 75°/0.5 mm. The residue, 106 g., which solidified upon refrigeration, was used for preparation of the bis(phthalimide) (XI), below. For purification, a portion of the solidified residue was extracted with petroleum ether, the extract evaporated to dryness and the residue crystallized from 2-propanol. Including material isolated by concentration of the mother liquor, the total yield of the ferrocene, m.p. 38–41°, was 39%. An analytical sample, m.p. 41–42°, was prepared by two recrystallizations from 2-propanol.

*Anal.* Calcd. for $C_{16}H_{24}Cl_2FeSi_2$: C, 48.13; H, 6.06; Cl, 17.76; Fe, 13.99. Found: C, 48.08; H, 5.92; Cl, 17.15; Fe, 14.05.

In an initial experiment an attempt was made to purify the compound by distillation, but decomposition was evident, and the orange-brown fraction, b.p. 125–135°/0.1 mm., contained 13.4% chlorine.

*1,1′-Bis(phthalimidomethyldimethylsilyl)ferrocene* (XI). A mixture of 231 g. (0.58 mole) of crude X and 236 g. (1.27 mole) of potassium phthalimide in 800 ml. of dimethylformamide was stirred at 90–110° for 4 hr., cooled, and filtered. Solvent was evaporated from the filtrate, and the residue was extracted with benzene. Removal of solvent from the extract and recrystallization of the resulting residue from 2-propanol furnished 198 g. (55%) of crude XI, m.p. 145–149°. After two recrystallizations, the product was analyzed. *Anal.* Found: N, 4.6%. In an initial experiment on a smaller scale, the yield of material m.p. 143–145° was 35%, and recrystallized XI melted 149–150°.

*Anal.* Calcd. for $C_{32}H_{32}FeN_2O_4Si_2$: C, 61.93; H, 5.20; N, 4.52. Found: C, 61.55; H, 5.37; N, 4.74.

*1,1′-Bis(aminomethyldimethylsilyl)ferrocene dihydrochloride* (XII). To a refluxing slurry of 192 g. (0.311 mole) of XI and 700 ml. of methanol was added 74 g. (1.26 moles) of 85% hydrazine hydrate. Refluxing was continued overnight. Concentrated hydrochloric acid (105 ml.; 1.06 moles) was then added dropwise during a 30-min. period, and refluxing was continued an additional 2 hr. The mixture was cooled, filtered, and the filtrate stripped of solvent. Extraction with benzene caused the residue to crystallize. The crystals were dissolved in water, the solution filtered, and the filtrate extracted with chloroform. The aqueous solution was evaporated to dryness. The residue was dissolved in hot methanol, the solution cooled and filtered to remove hydrazine hydrochloride, and the methanol evaporated from the filtrate; this procedure was repeated three times. Finally, the product was recrystallized from 2:1 2-propanol-methanol to give 108.3 g. (81%) of XII. It decomposed above 185°, without melting.

*Anal.* Calcd. for $C_{16}H_{30}Cl_2FeN_2Si_2$: C, 44.35; H, 6.98; Cl, 16.36; N, 6.47. Found: C, 44.45; H, 6.77; Cl, 16.71; N, 6.91.

*Acknowledgment.* We wish to thank Drs. H. Rosenberg and C. Tamborski of Wright Air Development Division, and Dr. K. C. Frisch, Polymer Research Department, Wyandotte Chemicals Corporation, for their interest and helpful discussions.

WYANDOTTE, MICH.

---

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

[18] Peninsular ChemResearch, Inc., Gainesville, Fla.