oil on 275 g. of acid-washed alumina using elution by 6:1 chloroform–carbon tetrachloride gave forty fractions (3.72 g.) of gummy solid with an overall melting range of 56–92.5°; only two significant peaks resulted. The last sixteen fractions (2.20 g., m.p. 61–92.5°) when combined and recrystallized from carbon tetrachloride gave 1.30 g. of material, m.p. 77–91°. Recrystallization from benzene-hexane gave 1.08 g. (40% recovery of the carbinol VIII), m.p. 87.5–91°, undepressed by authentic VIII; the infrared spectrum was essentially identical with that of VIII. A second crop amounted to 0.22 g., m.p. 62–70°.

The first twenty-four fractions (1.52 g.) when combined and recrystallized from carbon tetrachloride amounted to 0.45 g., m.p. 68–73°, which was not a carbinol (no infrared absorption in excess of 3130 cm.$^{-1}$) and was not studied further.

In the study simply of metalation of the carbinol VIII, 1.00 g. in 35 ml. of dry benzene was treated at *ca.* 25° with 0.004 mole of XII in apparatus attached through a Dry Ice trap to a wet test meter. No gas evolution occurred after addition of this first portion of XII. An additional 0.006 mole of XII was added and the mixture was heated rapidly to the reflux temperature. In 5 min., 0.07 l. of gas was collected (82% of theory for replacement of one hydrogen atom of VIII; the volume of gas reported here and subsequently is corrected to standard conditions); there was no further evolution during an additional heating period of 55 min. The mixture was cooled to 25°, hydrolyzed, and extracted with benzene. Removal of solvent gave 1.00 g. (100%) of material, m.p. 81–92°, undepressed by authentic VIII; the infrared spectrum was essentially identical with that of VIII.

In the second reaction with benzaldehyde, 5.00 g. of VIII was dissolved in 75 ml. of dry benzene at the reflux temperature, and 0.02 mole of XII was added rather rapidly. Gas evolution began almost immediately. The mixture was heated at the reflux temperature for 1 hr. and cooled to 25°. The gas evolved amounted to 0.35 l. (82% of theory for the replacement of one hydrogen atom), nearly all of which appeared in the first 5 min. of reflux. A second portion of the XII (0.03 mole) was added and the mixture was heated again to the reflux temperature and maintained at this temperature until gas evolution ceased (1.5 hr.). The additional gas evolved amounted to 0.15 l. (total evolution, 58% of theory for replacement of two hydrogen atoms). The mixture was cooled to 25° and 2.65 g. of purified benzaldehyde in 25 ml. of dry benzene was added. A gummy mass was formed which had to be dislodged occasionally from the sides and bottom of the flask. The mixture was stirred for 4.5 hr. at 25°. After hydrolysis, extraction with benzene, and removal of the solvent, there remained 7.1 g. of material, m.p. 78–88°. A portion of this material (3.00 g.) when triturated with cold carbon tetrachloride and twice recrystallized from carbon tetrachloride gave 1.86 g. of the original carbinol VIII, m.p. 91.5–93°, undepressed by authentic VIII; the infrared spectrum of the recrystallized VIII was identical with that of authentic material. Based on the total amount of product, the recovery of VIII was 88%.

NASHVILLE 5, TENN.

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

Ferrocenes. II. Silicon-Substituted Ferrocenes with Hydrolyzable Functional Groups[1,2]

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Silicon-substituted ferrocenes containing hydrolyzable functional groups were prepared from cyclopentadienyldimethylethoxysilane, cyclopentadienylmethyldiethoxysilane, cyclopentadienyldimethyl(1-piperidyl)silane, and 1-cyclopentadienyl-5-ethoxyhexamethyltrisiloxane. Hydrolysis of ethoxysilylferrocenes yielded bridged ferrocenes. Bridged compounds were also isolated when two bis(cyclopentadienyl)siloxanes were converted to ferrocenes.

A number of silicon-substituted ferrocenes are described in the literature,[3] but none contain hydrolyzable functional groups. In view of the importance of difunctional silanes for the preparation of silicones, it was of interest to prepare and hydrolyze compounds such as 1,1′-bis(dimethylethoxysilyl)ferrocene (II).

The preparation of cyclopentadienyldimethylethoxysilane (I), cyclopentadienylmethyldiethoxysilane, and 1-cyclopentadienyl-5-ethoxyhexamethyltrisiloxane was accomplished in 82–86% yields by treatment of the corresponding chloro compounds[4] with the required amount of ethanol in the presence of pyridine.

For the conversion of cyclopentadienyldimethylethoxysilane (I) to the corresponding ferrocene, II, conditions found to be effective were addition of isopropylmagnesium chloride to the cyclopentadienyl compound in tetrahydrofuran at 0°, and, after one hour, treatment of the resulting chloromagnesium derivative with ferrous chloride (62% yield). When *n*-butyllithium or phenyllithium was used in place of isopropylmagnesium chloride, the yield was low and the reaction less straightforward. With butyllithium, analysis of the product indicated that some replacement of ethoxy groups by butyl groups had occurred, a side reaction anticipated in view of the ready attack of ethoxysilanes by organolithium compounds.[5]

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[1] Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 1959.

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

[3] See R. L. Schaaf, P. T. Kan, C. T. Lenk, and E. P. Deck, *J. Org. Chem.*, 25, 1986 (1960), and references cited therein.

[4] Schaaf *et al.*, *J. Org. Chem.*, 25, 1986 (1960), and references cited therein.

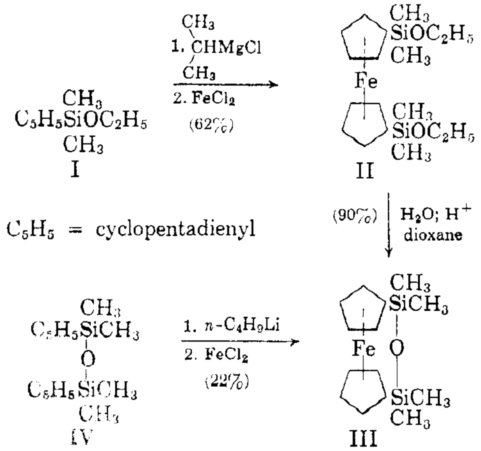
[5] H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, 68, 1675 (1946).

The selectivity of isopropylmagnesium chloride[6] was further shown by the conversion of cyclopentadienylmethyldiethoxysilane with this reagent and ferrous chloride to the tetrafunctional compound, 1,1'-bis(methyldiethoxysilyl)ferrocene (V), in 57% yield. Similarly, 1,1'-bis[dimethyl(1-piperidyl)silyl]ferrocene was formed from cyclopentadienyldimethyl(1-piperidyl)silane, but in this case the reaction with isopropylmagnesium chloride required more than one hour for completion.

Although isopropylmagnesium chloride could be used to advantage in the above-mentioned instances, application to 1-cyclopentadienyl-5-ethoxyhexamethyltrisiloxane did not produce ferrocenes upon addition of ferrous chloride. On the other hand, when butyllithium and ferrous chloride were used, 1,1'-bis(5-ethoxyhexamethyltrisiloxanyl)ferrocene was isolated in 23% yield.[7]

Hydrolysis of 1,1'-bis(dimethylethoxysilyl)ferrocene (II) in dioxane solution with an acid catalyst produced a bridged compound, 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane[8] (III), in 90% yield. The formation of a nonpolymeric bridged compound in high yield from a disubstituted ferrocene has been encountered previously in the preparation of the copper chelate of 1,1'-bis(α-benzoylacetyl)ferrocene.[9]

The same bridged disiloxane, III, was formed in 22% yield when 1,3-bis(cyclopentadienyl)tetramethyldisiloxane (IV) was treated with two equivalents of butyllithium and one equivalent of ferrous chloride. Admixture melting point and comparison of infrared spectra of samples prepared by the two routes proved their identity. A molecular weight determination eliminated an alternative dimeric structure. The bis(cyclopentadienyl)disiloxane used in this sequence was prepared from cyclopentadienyldimethylchlorosilane[4] by treatment with half an equivalent of water. When one equivalent of water was used, the subsequent addition of dimethyldichlorosilane furnished the corresponding trisiloxane, 1,5-bis(cyclopentadienyl)hexamethyltrisiloxane. Conversion of this compound to ferrocenes gave a 6% yield of a bridged trisiloxane, 1,5-(1,1'-ferrocenylene)hexamethyltrisiloxane,[10] along with a liquid mixture, b.p. 220–240°/0.07 mm., in an estimated 20% yield. In a related study, Luttringhaus and Kullick reported that treatment of the disodium derivatives of 1,3-bis(cyclopentadienyl)propane, 1,4-bis(cyclopentadienyl)butane, and 1,5-bis(cyclopentadienyl)pentane with ferric chloride produced chain polymers along with small amounts (0.025 to 2.5%) of bridged compounds.[11]



As in the case of the difunctional ferrocene, II, hydrolysis of the tetrafunctional ferrocene, V, produced a disiloxane bridge connecting the cyclopentadienyl rings. By hydrolysis with one equivalent of water in dioxane, a difunctional compound, 1,3-(1,1'-ferrocenylene)-1,3-dimethyl-1,3-diethoxydisiloxane (VI), was prepared in 77% yield. Subsequent hydrolysis of this product at 80° produced in 70% yield a cyclotetrasiloxane with two ferrocenylene substituents: namely, 2,4-(1,1'-ferrocenylene)-6, 8-(1,1'-ferrocenylene)-2,-4,6,8-tetramethylcyclotetrasiloxane (VII). Elemental analyses, molecular weight determinations, and the absence of hydroxyl bands in the infrared spectrum supported the cyclotetrasiloxane structure.

Inasmuch as the bridged difunctional intermediate, VI, possessed two asymmetric centers, hydrolysis could conceivably give rise to several stereoisomeric cyclotetrasiloxanes, and, indeed, when hydrolysis was conducted at 25°, the cyclotetrasiloxane fraction was not sharp melting. When hydrolysis was performed at 80°, on the other hand, the cyclotetrasiloxane VII melted at 270–276°, which indicated the predominance of one isomer, inasmuch as the pure material melted at 276°. Of the available structures for VII, m.p. 276°, the two plausible ones are the "*cis*" structure in which both ferrocenylene groups are attached to the same side of the cyclotetrasiloxane ring and the structure in which one ferrocenylene group is *trans* to the other. Hydrolysis at 25° gave, in addi-

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[6] For a discussion of steric effects in Grignard couplings with alkoxysilanes, see P. D. George, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, 77, 6647 (1955).

[7] When 1-cyclopentadienyl-3-ethoxytetramethyldisiloxane was treated with butyllithium and ferrous chloride, the crude ferrocene was formed, but some replacement of ethoxy groups by butyl groups also took place, according to results of elemental analysis of the twice-distilled product.

[8] The term "1,1'-ferrocenylene" is used to designate the diradical —C_5H_4—Fe—C_5H_4— in analogy with the common use of phenylene.

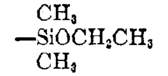
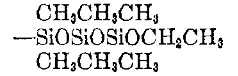
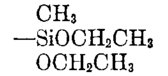
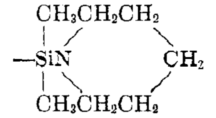
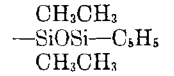
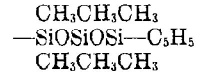
[9] C. R. Hauser and C. E. Cain, *J. Org. Chem.*, 23, 1142 (1958).

[10] This compound was the major product formed by hydrolysis of crude 1,1'-bis(3-ethoxyhexamethyltrisiloxanyl)ferrocene at 25° in dioxane in the presence of a small amount of acid catalyst (42% yield, 29% conversion). When the hydrolysis was conducted at 80°, the bridged disiloxane, III, was obtained.

[11] A. Luttringhaus and W. Kullick, *Angew. Chem.*, 70, 438 (1958).

TABLE I

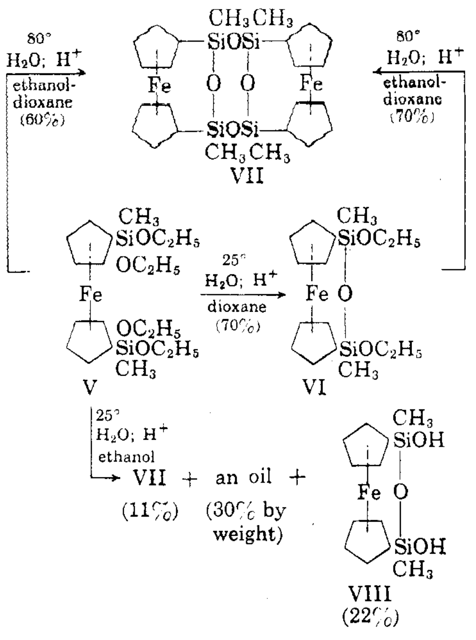
SILICON-SUBSTITUTED CYCLOPENTADIENES, $C_5H_5—R$

No.	R[a]	Formula	Yield, %	B.P., /mm.	n_D^{25}	Carbon, %		Hydrogen, %		Silicon, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
1	 $\overset{CH_3}{\underset{CH_3}{—SiOCH_2CH_3}}$	$C_9H_{16}OSi$	86	34–38/2.5	1.4564	64.22	64.30	9.58	9.55	16.69	16.76
2	 $\overset{CH_3CH_3CH_3}{\underset{CH_3CH_3CH_3}{—SiOSiOSiOCH_2CH_3}}$	$C_{13}H_{28}O_3Si_3$	82	70–72/0.5	1.4268	49.31	49.24	8.91	8.87	26.62	26.64
3	 $\overset{CH_3}{\underset{OCH_2CH_3}{—SiOCH_2CH_3}}$	$C_{10}H_{18}O_2Si$	86	40–45/0.8	1.4452	60.56	59.96	9.15	9.27	14.16	13.94
4		$C_{12}H_{21}NSi$	82	56–60/0.3	1.4984	69.49	68.74	10.21	10.42	13.55 6.75[b]	13.96 7.01[b]
5	 $\overset{CH_3CH_3}{\underset{CH_3CH_3}{—SiOSi—C_5H_5}}$	$C_{14}H_{22}OSi_2$	53	65/0.15	1.4852	64.07	63.87	8.43	8.63	21.40	21.33
6	 $\overset{CH_3CH_3CH_3}{\underset{CH_3CH_3CH_3}{—SiOSiOSi—C_5H_5}}$	$C_{16}H_{28}O_2Si_3$	49	89–94/0.2	1.4708	57.08	56.99	8.38	8.23	25.03	24.87

[a] C_5H_5 = cyclopentadienyl. [b] Nitrogen, %.

tion to the cyclotetrasiloxane mixture (22%), a siloxanediol, 1,3-(1,1′-ferrocenylene)-1,3-dimethyl-1,3-dihydroxydisiloxane (VIII), in 24% yield.

The cyclotetrasiloxane, VII, m.p. 274–276°, was also obtained in 60% yield directly from the tetrafunctional compound (V) by hydrolysis at 80° with an excess of water. When hydrolysis was conducted at 25°, three fractions were isolated: the cyclotetrasiloxane, VII (11%), m.p. 275–276°; the siloxanediol, VIII (24%); and a hydroxyl-containing oil, believed to be a low-molecular-weight ferrocenylsiloxane polymer (30% by weight).



Results from the hydrolysis of 1,1′-bis(5-ethoxyhexamethyltrisiloxanyl)ferrocene were inconclusive, but from the low yield of nonvolatile material isolated it appeared that cleavage of the siloxane chain had taken place (*cf.* footnote 10).

1,1′-Bis(dimethylethoxysilyl)ferrocene (II) reacted with phenyldimethylchlorosilane at 200° in the presence of ferric chloride catalyst with the evolution of ethyl chloride,[12] but the major product was not the anticipated 1,1′-bis(3-phenyltetramethyldisiloxanyl)ferrocene. The bridged disiloxane, III, was isolated in 58% yield.

In accordance with the assigned structures, the infrared spectra of the above bridged siloxanes did not show bands near 1000 or 1110 cm.$^{-1}$, one or both of which are present when one cyclopentadienyl ring is unsubstituted.[13] One exception was the spectrum of compound VI, which had a strong band at 1110 cm.$^{-1}$, also present in the spectrum of the precursor V. The spectra of the bridged siloxanes showed strong bands between 1015 and 1090 cm.$^{-1}$, characteristic of the siloxane linkage.[14]

EXPERIMENTAL[15]

Cyclopentadienylethoxysilanes and cyclopentadienylethoxysiloxanes (Compounds 1–8, incl., Table I). The method for the preparation of the ethoxy compounds listed in Table I is illustrated by the synthesis of cyclopentadienyldimethylethoxysilane (I) (compound 1, Table I). A solution of 655 g. (4.13 moles) of cyclopentadienyldimethylchlorosilane[4] in 6 l. of ether was stirred under nitrogen in an ice bath. Pyridine (327 g.; 4.13 moles) was added in one portion and was followed by dropwise addition of 190 g. (4.13 moles) of ethanol.

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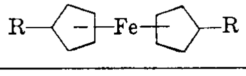
[12] P. C. Servais, U. S. Patent 2,485,928 (Oct. 25, 1949).

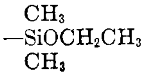
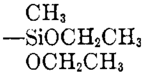
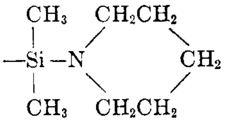
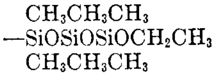
[13] M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958); M. Rosenblum, Ph.D. Thesis, Harvard University, August 1953.

[14] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Methuen and Co., Ltd., London, 1958, p. 334.

TABLE II

SILICON-SUBSTITUTED FERROCENES



No.	R	Formula	Yield, %	B.P., /mm.	n_D^{25}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Iron, % Calcd.	Iron, % Found
1	 $-\overset{CH_3}{\underset{CH_3}{Si}}OCH_2CH_3$	$C_{18}H_{30}FeO_2Si_2$	62	104–109/0.03[a]	1.5262	55.37	55.05	7.74	7.72	14.30	14.12
2	 $-\overset{CH_3}{\underset{OCH_2CH_3}{Si}}OCH_2CH_3$	$C_{20}H_{34}FeO_4Si_2$	57[b]	138–141/0.15	1.5076	53.32	53.69	7.61	7.44	12.40	12.43
3		$C_{24}H_{40}FeN_2Si_2$	69	187–195/0.08	1.5556	61.51	61.33	8.60	8.43	11.92 5.98[c]	11.53 5.38[c]
4	 $-\overset{CH_3}{\underset{CH_3}{Si}}O\overset{CH_3}{\underset{CH_3}{Si}}O\overset{CH_3}{\underset{CH_3}{Si}}OCH_2CH_3$	$C_{26}H_{54}FeO_6Si_6$	23	164–170/0.05	1.4672	45.45	45.87	7.92	8.04	8.13	8.03

[a] M.p. 15.5–19°. [b] After two distillations; in addition, 18% of the starting material was recovered. [c] Nitrogen, %.

The mixture was stirred overnight, filtered, the solid washed with petroleum ether, and the filtrate evaporated *in vacuo*. Distillation of the residue through a 20-cm. Vigreux column furnished the ethoxysilane (I), b.p. 34–38°/2.6 mm., in 81 to 86% yields. Compounds 1 and 2 were redistilled before analysis.

For the preparation of the diethoxysilane, compound 3, the addition of pyridine and ethanol was followed by a second equivalent of each, in the same order. In addition to the main distillation fraction (68%), which was analyzed, there was obtained a second fraction, b.p. 45–75°/0.8 mm., which upon redistillation furnished 18% of the diethoxysilane, b.p. 35–40°/0.6 mm., n_D^{25} 1.4481.

Cyclopentadienyldimethyl(1-piperidyl)silane (*Compound 4, Table I*). By the substitution of 2 moles of piperidine for one each of pyridine and ethanol, the above procedure for the preparation of compound 1 furnished compound 4, Table I.

1,3-Bis(cyclopentadienyl)tetramethyldisiloxane (IV) (*Compound 5, Table I*). A solution of 31.7 g. (0.2 mole) of cyclopentadienyldimethylchlorosilane in 250 ml. of anhydrous ether was stirred at −30° under nitrogen while first pyridine (15.8 g.; 0.2 mole) and then water (1.9 ml.; 0.105 mole) was added dropwise. The mixture was allowed to come to room temperature with stirring overnight, it was filtered, and the solid was washed with ether. Solvent was removed from the filtrate *in vacuo*, the residue was distilled, and the fraction (18.5 g.) which boiled at 57–75°/0.12 mm. was redistilled through a 25-cm. column to give compound 5, Table I.

1,5-Bis(cyclopentadienyl)hexamethyltrisiloxane (*Compound 6, Table I*). A solution of 115.4 g. (0.726 mole) of cyclopentadienyldimethylchlorosilane in a mixture of 300 ml. of ether and 300 ml. of dioxane was stirred under nitrogen in an ice bath while 114.8 g. (1.45 moles) of pyridine was added. After 10 min., a solution of 13.1 g. (0.726 mole) of water in a mixture of 150 ml. of ether and 150 ml. of dioxane was added in one portion and followed 15 min. later by 46.8 g. (0.363 mole) of dimethyldichlorosilane in 100 ml. of ether, added in a slow stream. The ice bath was removed and the mixture stirred overnight at room temperature. The precipitated pyridine hydrochloride was removed by filtration, the solvent evaporated under vacuum, and the residue distilled. Compound 6, Table I, was obtained by redistillation of the fraction (59 g.; 49%) which was collected at 90–105°/0.25 mm.

Silicon-substituted ferrocenes listed in Table II. Compounds 1, 2, and 3, Table II, were prepared by procedures represented by Method A, below, in which the synthesis of compound 1 is described. Compound 4 was prepared by Method B.

Method A. A solution of isopropylmagnesium chloride was prepared by dropwise addition of 100 ml. of isopropyl chloride to 27 g. (1.1 moles) of magnesium in 250 ml. of ether, after the reaction had been initiated by a mixture of 3 ml. of isopropyl bromide and 25 ml. of isopropyl chloride. A solution of 168 g. (1 mole) of cyclopentadienyldimethylethoxysilane (I) in 1 l. of anhydrous tetrahydrofuran was stirred under nitrogen in an ice bath until cold, and the isopropylmagnesium chloride solution was then added during a 15-min. period. After the mixture was stirred 1 hr. further in the ice bath, a slurry of ferrous chloride, prepared[16] from 54.2 g. (0.333 mole) of ferric chloride and 9.40 g. (0.168 g.-atom) of iron powder in 200 ml. of tetrahydrofuran, was added in four portions. 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. Evaporation of the extract and subsequent distillation furnished 121 g. (62%) of 1,1′-bis(dimethylethoxysilyl)ferrocene (II), b.p. 131–132°/0.4 mm., m.p. 14.5–17°. It was redistilled for analysis (compound 1, Table II).

Application of Method A to compound 4, Table I, produced compound 3, Table II, in 22% yield. However, when the mixture of isopropylmagnesium chloride and cyclopentadienyl compound was stirred for 6 hr. at room temperature before addition of ferrous chloride, the yield rose to 69%.

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(15) All melting points and boiling points are uncorrected. Melting points were determined in sealed capillaries which had been flushed with nitrogen. Analysis for iron, performed in this laboratory by Mr. Peter A. Marsh, involved fusion with sodium peroxide in a Parr bomb, acidification, reduction *via* a Jones' reductor, and titration with ceric sulfate. Other analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y. Distillations were in general conducted under nitrogen.

(16) G. Wilkinson, *Org. Syntheses*, **36**, 31 (1956).

An attempt to prepare compound 4, Table II, by Method A gave no sharp-boiling materials, and the liquid fractions did not have the characteristic orange-brown color of siloxanylferrocenes.

Method B. A solution of *n*-butyllithium prepared[17] from 22.5 g. (0.164 mole) of *n*-butyl bromide was added dropwise to 52 g. (0.164 mole) of 1-cyclopentadienyl-5-ethoxyhexamethyltrisiloxane (compound 2, Table I) in 250 ml. of tetrahydrofuran with stirring under nitrogen in an ice bath. After the mixture was stirred for 1 hr., a slurry of ferrous chloride, prepared[16] from 8.9 g. (0.055 mole) of ferric chloride and 1.26 g. of iron powder in tetrahydrofuran, was added and the mixture stirred overnight. Solvent was removed by vacuum evaporation, and benzene was added to the residue. Petroleum ether was then added, the mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was extracted with benzene and petroleum ether, and the extracts were combined and distilled. The fraction (19.5 g.) which boiled at 168–190°/0.37 mm. was redistilled to give 13 g. (23%) of compound 4, Table II.

When applied to 16.8 g. (0.1 mole) of cyclopentadienyldimethylethoxysilane (I), Method B produced a small amount of ferrocene and an orange-brown liquid, which was collected in two distillation fractions: 6.0 g., b.p. 97–120°/0.01 mm., and 2.6 g., b.p. 120–124°/0.01 mm., n_{D}^{25} 1.5244. Analysis of the second fraction indicated that the ethoxy groups in the product (II) were in part replaced by butyl groups.

Anal. Calcd. for $C_{18}H_{30}FeO_2Si_2$: C, 55.37; H, 7.74. Calcd. for $C_{20}H_{34}FeOSi_2$: C, 59.67; H, 8.51. Found: C, 57.71, 57.82; H, 7.82, 8.03.

When the reaction was performed at −50° on a 0.1-mole scale, distillation of the final extract gave a little sublimed ferrocene and 7.7 g. of an orange-brown liquid, b.p. 110–124°/0.05 mm. When phenyllithium was used in place of *n*-butyllithium at 0° and the mixture stirred 30 min. before addition of ferrous chloride, ferrocene was isolated along with 2.3 g. of a colored liquid, b.p. 101–132°/0.09 mm.

1,3-(1,1′-Ferrocenylene)-1,3-dimethyl-1,3-diethoxydisiloxane (VI). To 15.0 g. (0.033 mole) of 1,1′-bis(methyldiethoxysilyl)-ferrocene (V) in 100 ml. of dioxane was added 10 ml. of a solution of 5.4 g. (0.33 mole) of water and 3 drops of concd. hydrochloric acid in 100 ml. of dioxane. After 20 hr., distillation yielded 13.9 g. of liquid, predominantly starting material, b.p. 123–137°/0.02 mm. This liquid was dissolved in 30 ml. of dioxane, treated with 0.4 g. of water and 3 drops of concd. hydrochloric acid and allowed to stand for 6 days. Removal of solvent *in vacuo* and distillation of the residue furnished 9.6 g. (77%) of the bridged diethoxy compound (VI), b.p. 128–131°/0.4 mm., n_{D}^{25} 1.5396.

Anal. Calcd. for $C_{16}H_{24}FeO_3Si_2$: C, 51.06; H, 6.43; Fe, 14.84. Found: C, 51.06, 51.19; H, 6.37, 6.35; Fe, 15.11, 14.91.

Hydrolysis of 1,1′-bis(dimethylethoxysilyl)ferrocene (II). *1,3-Bis(1,1′-ferrocenylene)tetramethyldisiloxane* (III). To a mixture of 118 g. (0.3 mole) of II, 275 ml. of dioxane, and 11 ml. (0.61 mole) of water was added 2.8 ml. of concd. hydrochloric acid. The solution was allowed to stand for 24 hr., and then solvent was removed by evaporation under vacuum. Extraction of the residue with a small amount of methanol left 73.8 g. of the bridged compound, III, m.p. 86–88°. Evaporation of the extract and recrystallization of the resulting residue from 2-propanol furnished an additional 11.0 g. of the bridged compound, m.p. 86–87°; total yield, 90%. The product was identified by mixture melting point and infrared comparison with material prepared as described below from 1,3-bis(cyclopentadienyl)-tetramethyldisiloxane.

Hydrolysis of 1,1′-bis(5-ethoxyhexamethyltrisiloxanyl)ferrocene. This ferrocene (1.51 g., 0.0022 mole) in 6 ml. of dioxane was hydrolyzed with 4 drops of 20% hydrochloric acid. After 5 days, the solvent was removed *in vacuo*, and the residue, in petroleum ether, was chromatographed on 40 g. of alumina ("WOELM" nonalkaline, activity grade 1). By elution with 200 ml. of petroleum ether, 0.095 g. of solid, m.p. 50–65° was obtained. Material isolated by elution with 200 ml. of petroleum ether-benzene (4:1), 100 ml. of benzene followed by 200 ml. of ether, and finally 200 ml. of methanol weighed 0.079 g., 0.025 g., and 0.213 g., respectively. After the final elution, the column was pale green, the majority of colored materials having been removed.

Hydrolysis of 1,3-(1,1′-ferrocenylene)-1,3-dimethyl-1,3-diethoxydisiloxane (VI). 1. *At 25°.* A mixture of 1.0 g. (0.0027 mole) of the ferrocene (VI), 3 ml. of water, 12 ml. of ethanol, and 1 ml. of concd. hydrochloric acid was allowed to stand for 2 hr. Crystals which formed were collected by filtration, washed with water, and recrystallized from 2-butanone, but this cyclotetrasiloxane mixture, 0.12 g., did not melt sharply (shrinks below 265°, m.p. up to 275°). The combined filtrate and wash was extracted with ether, the ether layer washed with water and then evaporated to dryness, *in vacuo*. Extraction of the residue with benzene left a solid which, after recrystallization from chloroform, weighed 0.21 g. (24%), m.p. 162–165°, undepressed by admixture with 1,3-(1,1′-ferrocenylene)-1,3-dimethyl-1,3-dihydroxydisiloxane (VIII) (below). Evaporation of the benzene extract left 0.23 g. of an oil.

2. *At 80°.* A mixture of 3.0 g. (0.0080 mole) of VI, 1.5 g. (0.083 mole) of water, 3 ml. of ethanol, 5 ml. of dioxane, and 6 drops of concd. hydrochloric acid was refluxed for 4 hr. The mixture was then refrigerated overnight. By filtration and washing with ethanol, 1.69 g. (70%) of crude VII, m.p. 271–276°, was obtained. After two recrystallizations from 2-butanone, the product *2,4-(1,1′-ferrocenylene)-6,8-(1,1′-ferrocenylene)-2,4,6,8-tetramethylcyclotetrasiloxane* (VII), melted at 276°.

Anal. Calcd. for $C_{24}H_{28}Fe_2O_4Si_4$: C, 47.69; H, 4.67; Fe, 18.48; mol. wt., 604. Found: C, 48.05, 48.15; H, 4.69, 4.61; Fe, 18.70; mol. wt. (camphor), 670, 714, 692.

Hydrolysis of 1,1′-bis(methyldiethoxysilyl)ferrocene (V). 1. *At 25°.* The above procedure for the hydrolysis of the bridged diethoxy compound (VI) at 25° was employed, with the exception that the initial extraction solvent was benzene instead of ether. Material obtained by recrystallization from 2-butanone melted at 275–276° (VII, 11%). Material obtained by recrystallization from chloroform was *1,3-(1,1′-ferrocenylene)-1,3-dimethyl-1,3-dihydroxydisiloxane* (VIII) (21%), m.p. 163.5–165° dec.; an additional recrystallization did not alter the melting point.

Anal. Calcd. for $C_{12}H_{16}FeO_3Si_2$: C, 45.01; H, 5.04; Fe, 17.44; Si, 17.52; mol. wt., 320. Found: C, 45.32; H, 5.12; Fe, 17.36; Si, 17.56; mol. wt. (Signer-Barger), 300, 304.

The infrared spectrum of this compound showed strong bands at 3100–3200 cm.$^{-1}$ and at 875–885 cm.$^{-1}$ (silanol), and showed strong bands in the siloxane region at 1010–1040 cm.$^{-1}$ In contrast, the spectrum of an oil (30% by weight) isolated by evaporation of the final benzene extract showed a strong silanol band at 3340 cm.$^{-1}$, and bands beyond 1100 cm.$^{-1}$ were not sharp.

2. *At 80°.* The procedure given above for the hydrolysis of the difunctional bridged compound, VI, at 80° was employed. The cyclotetrasiloxane (VII), m.p. 274.5–276°, was obtained in 60% yield, after one recrystallization from 2-butanone.

Reaction of 1,3-bis(cyclopentadienyl)tetramethyldisiloxane) with n-butyllithium and ferrous chloride. *n*-Butyllithium solution prepared[17] from 35.9 g. (0.26 mole) of *n*-butyl bromide was added during a 30-min. period with stirring to 34.5 g. (0.131 mole) of 1,3-bis(cyclopentadienyl)tetramethyldisiloxane in 400 ml. of anhydrous ether under a blanket of nitrogen. Anhydrous tetrahydrofuran (300 ml.) was then added and the mixture stirred at room temperature for 2.5 hr. A slurry of ferrous chloride prepared[16] from 14.2 g. of ferric chloride and 2.5 g. of iron powder in tetrahydrofuran was added slowly; solvent was then removed by distillation until the head temperature reached 55°. After the

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

mixture was refluxed overnight, it was distilled to dryness, *in vacuo*, toluene added, salts removed by filtration, and the filtrate distilled. Most of the high-boiling material (14.9 g., b.p. 68–86°/0.07–0.15 mm.) solidified during distillation. Recrystallization from heptane yielded 7.1 g. of crude III, m.p. 83–88°. After two additional crystallizations, the compound, *1,3-(1,1′-ferrocenylene)tetramethyldisiloxane* (III), melted at 87–88°.

Anal. Calcd. for $C_{14}H_{20}FeOSi_2$: C, 53.16; H, 6.38; Fe, 17.66; Si, 17.74; mol. wt. 316. Found: C, 52.88; H, 6.08; Fe, 17.87; Si, 17.47; mol. wt. (camphor), 281.

Extraction of the distillation residue with heptane furnished an additional 1.9 g. of the bridged compound (III), m.p. 87–88°; total yield, 22%.

In a second experiment the cyclopentadiene compound was treated with 1 equivalent of *n*-butyllithium and then followed successively with ferrous chloride, *n*-butyllithium, and again ferrous chloride under conditions similar to those used in the previous experiment. By distillation, crude 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane, m.p. 79–86°, was isolated in 20% yield, and after several recrystallizations from 2-propanol, it melted at 87.5–88°.

Reaction of 1,5-bis(cyclopentadienyl)hexamethyltrisiloxane with n-butyllithium and ferrous chloride. A solution of *n*-butyllithium prepared[17] from 0.274 mole of *n*-butyl bromide was added to 46 g. (0.137 mole) of 1,5-bis(cyclopentadienyl)-hexamethyltrisiloxane in 100 ml. of tetrahydrofuran under nitrogen during a 20-min. period. After the mixture had stirred for 1.5 hr., a slurry of ferrous chloride prepared[16] from 0.092 mole of ferric chloride and 0.046 mole of iron powder was added, followed by 250 ml. of tetrahydrofuran. The mixture was refluxed overnight, solvent removed *in vacuo*, and the residue extracted thoroughly with benzene. The extract was washed with water (emulsion), filtered, and the benzene layer taken to dryness. Lower-boiling components in the resulting residue were removed by distillation up to 105°/0.17 mm., the remainder was extracted with 2-propanol, and the extract was distilled. Solid material in a fraction (8 g.), b.p. 90–110°/0.02–0.1 mm., was recrystallized from 2-propanol, giving 2.9 g. (6%) of 1,5-(1,1′-ferrocenylene)hexamethyltrisiloxane, m.p. 73–75° (see below). A second distillation fraction (11 g.), b.p. 220–240°/0.07 mm., was redistilled, and the fraction (5 g.), b.p. 180–250°/0.02 mm., was analyzed; this material may be a mixture of 1,1′-bis(cyclopentadienylhexamethyltrisiloxanyl)ferrocene, $C_{32}H_{54}FeO_4Si_6$, and a cyclic compound, $C_{32}H_{52}Fe_2O_4Si_6$.

Anal. Calcd. for $C_{32}H_{54}FeO_4Si_6$: C, 52.85; H, 7.49; Fe, 7.68. Calcd. for $C_{32}H_{52}Fe_2O_4Si_6$: C, 49.21; H, 6.71; 14.30. Found: C, 49.53; H, 7.45; Fe, 10.14, 10.33, 10.14.

1,5-Bis(cyclopentadienyl)hexamethyltrisiloxane (20.5 g.) was treated also with 1 equivalent of *n*-butyllithium, followed successively with ferrous chloride, *n*-butyllithium, and again ferrous chloride. By distillation there was isolated 6.5 g. of a mixture of solid and liquid, b.p. 110–137°/0.28 mm., which after refrigeration and washing with 2-propanol yielded 1.3 g. of crystals, m.p. 55–67°. After two recrystallizations from 2-propanol, the solid, *1,5-(1,1′-ferrocenylene)hexamethyltrisiloxane*, melted at 73.5–75°.

Anal. Calcd. for $C_{16}H_{26}FeO_2Si_3$: C, 49.21; H, 6.71; mol. wt., 391. Found: C, 49.43; H, 6.69; mol. wt. (camphor), 397.

Treatment of 1,1-bis(dimethylethoxysilyl)ferrocene (II) *with phenyldimethylchlorosilane in the presence of ferric chloride.* A mixture of 3.90 g. (0.01 mole) of the diethoxy compound (II), 3.41 g. (0.02 mole) of phenyldimethylchlorosilane, and 0.07 g. of ferric chloride was heated in a bath at 200° during a 5-hr. period under nitrogen. A gas (ethyl chloride) which evolved was condensed in a trap at −70°. The mixture was cooled, 50 ml. of petroleum ether was added, and, after 20 hr., the mixture was filtered and the filtrate evaporated *in vacuo*. Distillation of the residue gave a solid fraction (2.33 g.), b.p. 85–92°/0.12 mm., which by recrystallization from 2-propanol yielded 1.54 g. (49%) of 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane (III), m.p. 87–88°; admixture melting with an authentic sample showed no depression. An additional 0.19 g. of the bridged compound, m.p. 86–87°, was recovered from the mother liquor, and 0.10 g., m.p. 85–87°, was precipitated from the distillation residue by addition of a small amount of petroleum ether and cooling to −70°; total yield, 58%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Di- and Tetrabenzylations of Mono- and Bisacetylferrocenes with Benzyl Chloride by Potassium Amide. Comparison with Acetophenone

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The methyl group of monoacetylferrocene was alkylated with benzyl chloride by means of potassium amide to form the dibenzylation product. Attempts to isolate the intermediate monobenzylation product were unsuccessful. Evidence was obtained that the second benzyl group was introduced into the molecule more rapidly than the first. Similarly the two methyl groups of bisacetylferrocene were alkylated with benzyl chloride by potassium amide to form the tetrabenzylation product. No intermediates were isolated. These alkylations furnish more convenient methods of syntheses of the corresponding di- and tetrabenzylation products than certain methods that were devised in connection with the proof of their structures. Certain theoretical aspects are considered. The results are compared with the benzylation of acetophenone.

Previous papers have described condensations of mono- and bisacetylferrocene with esters[2-4] and with benzaldehyde.[2,5] The present paper describes benzylations of these methyl ketones and also of acetophenone.

Results with monoacetylferrocene. This methyl ketone (I) was alkylated with benzyl chloride by means of potassium amide to form the dibenzyl

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