Anal. Calcd. for $C_{15}H_{16}$: MR_D, 64.80. Found: MR_D, 64.61.

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[CONTRIBUTION FROM THE MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Derivatives of Ferrocene. VI. Heteroannular Disubstitution of Ferrocene[1]

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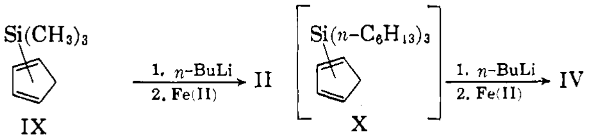
Confirmation of previous postulates regarding the steric course of two metalation reactions of ferrocene is presented. It is rigorously shown that treatment of ferrocene with *n*-butyllithium or with phenylsodium gives rise to 1,1′-dilithioferrocene or 1,1′-disodioferrocene, respectively. Dilithio- and disodioferrocene were converted to silyl derivatives which are identical to those obtained from reactions of correspondingly substituted cyclopentadienes and iron(II) chloride.

In a previous publication from this laboratory[2] some work concerning the metalation of ferrocene was described. Included in that report was the preparation of two silylferrocenes which were obtained from treatment of the reaction mixture of ferrocene and *n*-butyllithium with trimethylchlorosilane. Analytical values obtained from these products were consistent with a monosubstituted ferrocene, trimethylsilylferrocene (I), and a disubstituted ferrocene which was assigned the structure, 1,1′-bis(trimethylsilyl)ferrocene (II). The assignment had as its basis the absence of absorption near 9 and 10 μ in the infrared spectrum of the compound (9–10 Rule[3]).

	R_1	R_2
I.	$(CH_3)_3Si$—	H—
II.	$(CH_3)_3Si$—	$(CH_3)_3Si$—
III.	$(n\text{-}C_6H_{13})_3Si$—	H—
IV.	$(n\text{-}C_6H_{13})_3Si$—	$(n\text{-}C_6H_{13})_3Si$—
V.	Li—	H—
VI.	Li—	Li—
VII.	Na—	H—
VIII.	Na—	Na—

In the present study, treatment of the mixture of lithioferrocenes (V and VI) with tri-*n*-hexylbromosilane also yielded a mono- and disubstituted silylferrocene. The infrared spectra of both compounds, in this case, exhibited strong absorption at 9 and 10 μ. This observation, therefore, caused us to consider the correctness of the previous structural assignment for II.[2] The fact that the spectrum of tri-*n*-hexylbromosilane also showed strong absorption at 9 and 10 μ, could not, at first, be taken to mean that these bands were the ones present in the spectrum of IV since it was not possible to preclude the absence of 9–10 absorption due to the ferrocene nucleus of IV. Additional experimental work, however, conclusively showed both disubstituted silylferrocenes, II and IV, to possess heteroannular orientation; so that the absorption at 9 and 10 μ in the spectrum of IV was, in fact attributed to the substituents and not to a possible inconsistency with the 9–10 Rule.

The heteroannular locations of the silyl functions in II and IV were proven by synthesis of both compounds from the correspondingly substituted cyclopentadiene derivatives, IX and X.



Trimethylsilylcyclopentadiene (IX) was prepared according to the procedure reported by Frisch.[4] This material was treated with *n*-butyllithium followed by iron(II) chloride to yield 1,1′-bis(trimethylsilyl)ferrocene (II). The product gave rise to an infrared spectrum identical to that obtained from the disubstituted product previously prepared *via* lithiation of ferrocene.[2]

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(1) Presented before the Division of Organic Chemistry, 134th Meeting, ACS, Chicago, September 1958.

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

(3) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958); *cf.* M. Rosenblum, doctoral dissertation, Harvard University 1953.

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The tri-n-hexylsilylferrocenes, III and IV, were also prepared from the mixture of V and VI, but during the present investigation an improved method for the lithiation of ferrocene[5] was used. The extent of metalation was checked after 18 hr. by carbonation of an aliquot of the reaction mixture. The amount of ferrocenedicarboxylic acid thus obtained indicated a 56% conversion of ferrocene to VI. After treatment of the mixture with tri-n-hexylbromosilane and isolation of the products by means of chromatography on alumina, the relative amounts of III and IV obtained indicated that an incomplete reaction between VI and the bromosilane took place since an unaccountably large yield of III was isolated. Replacement of both lithio groups of VI by bulky tri-n-hexylsilyl radicals was probably attended with difficulty because of steric factors. The high yield of III was best explained by hydrolysis of the intermediate, 1-lithio-1′-tri-n-hexylsilylferrocene.

The same two products, III and IV, were also obtained from treatment of the reaction mixture of ferrocene and phenylsodium with tri-n-hexylbromosilane. Formation of III in this case may have also resulted from an incomplete reaction of disodioferrocene (VIII) with the bromosilane since it was reported[6] that a negligible quantity of monosodioferrocene (VII) is formed by the action of phenylsodium on ferrocene.

Unequivocal synthesis of IV was achieved by the preparation of tri-n-hexylsilylcyclopentadiene (X) (not isolated), and treatment of the latter with n-butyllithium followed by iron(II) chloride. Although IV was formed in small yield (4%), it was isolated in the pure state by means of chromatography on alumina. This authentic heteroannularly substituted compound possessed properties (infrared spectrum and refractive index) identical to those of the same two disubstituted products obtained *via* lithiation and sodiation of ferrocene.

The chemical evidence obtained in this work, which rigorously proves the structures II and IV and establishes the steric course of the two metalation reactions described, serves an additional purpose as well. The intermediates VI and VIII are directly relatable to 1,1′-diacetylferrocene through 1,1′-ferrocene dicarboxylic acid,[7] and the results of the present investigation, therefore, serve as further confirmation for the structures previously assigned to these compounds.[8]

EXPERIMENTAL[9]

1,1′-Bis(trimethylsilyl)ferrocene (III). Trimethylsilycyclopentadiene[4] (IX) (12.2 g.; 0.88 mole in 100 ml. of dry benzene) was added to a solution of n-butyllithium (125 ml. of a 0.70 molar solution in petroleum ether, b.p. 40–60°) during 30 min. The reaction mixture was heated under reflux during 1 hr. while it was kept under N_2. After the mixture had cooled to room temperature, anhydrous iron(II) chloride [prepared from 27 ml. of chlorobenzene and 9.7 g. of anhydrous iron(III) chloride[10]] was added as a slurry in 150 ml. of benzene. The petroleum ether was then removed by distillation, and 200 ml. of pure dry tetrahydrofuran (THF) was added in its place. After the reaction mixture was stirred overnight at room temperature, it was treated with ice water; and the THF removed by evaporation. The residue was filtered, and the filtrate phase-separated. Ether extracts of the aqueous phase, combined with the bulk organic phase obtained from the filtrate, were evaporated to a dark-colored oil which was fractionated *in vacuo*. The distillation yielded II(7.3 g.; 50% yield based on 0.88 mole of IX), n_D^{25} 1.5437, which was collected at 96–104° (0.04–0.15 mm.). This orange-red-colored oil gave rise to an infrared spectrum which was superimposable upon the spectrum obtained from the disubstituted product prepared *via* the lithiation of ferrocene.[2]

Tri-n-hexylsilylferrocenes. A. III and IV *via* lithiation of ferrocene.[6] n-Butyllithium (1100 ml. of a 0.88M ethereal solution), cooled to −10°, was added to ferrocene (35.0 g.; 0.19 mole in 1100 ml. of THF) which was stirred in an atmosphere of dry N_2. The solution of ferrocene was initially cooled to −35°. Addition of the solution of n-butyllithium, although carried out as fast as possible (15 min.), was made so that the temperature of the reaction mixture did not rise above −10°. Stirring was continued while the mixture was allowed to warm to room temperature (2 hr.), and the reaction was then kept at room temperature for an additional 18 hr. At that time an aliquot was withdrawn and treated with carbon dioxide (Dry Ice) to form ferrocenedicarboxylic acid. The amount of diacid obtained (304 mg.) indicated a 56% conversion of ferrocene to VI. The lithiation was allowed to continue for another 4 hr. (24 hr. total time), after which time tri-n-hexylbromosilane[11] (73.6 g.; 0.23 mole) was rapidly added. A mild exothermic reaction was observed during the addition. The reaction mixture, adequately protected from light and kept in an atmosphere of N_2, was stirred during 4 days at room temperature. Enough water was then added (200 ml.) to dissolve the solid material (presumed to be LiBr) which was deposited, and the dark orange-red mixture was heated on a steam bath until the odor of THF was no longer detected.

The residue was extracted with $CHCl_3$, and the extracts evaporated to a dark, red-brown, mobile oil which was subsequently heated *in vacuo* (90–100°) to sublime the un-

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(5) D. W. Mayo, P. D. Shaw, and M. Rausch, *Chem. & Ind.* (*London*), 1388 (1957).

(6) A. N. Nesmeyanov, E. G. Perevalova, and Z. A. Beinoravichute, *Doklady Akad. Nauk S. S. S. R.*, **112**, 439 (1957).

(7) Carbonation of VI by R. A. Benkeser, D. Goggin, and G. Schroll [*J. Am. Chem. Soc.*, **76**, 4025 (1954)], A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova [*Doklady Akad. Nauk S. S. S. R.*, **97**, 459 (1954)] and D. W. Mayo, P. D. Shaw, and M. Rausch (Ref. 5), and carbonation of VIII by A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova (above), produced a dicarboxylic acid (1,1,-ferrocenedicarboxylic acid) with properties identical to those of the diacid obtained by Rosenblum and Woodward (Ref. 3) through hypoiodite oxidation of diacetylferrocene-A (1,1,-diacetylferrocene).

(8) See, M. Rosenblum and R. B. Woodward, Ref. 3 and other work cited therein.

(9) All boiling points are uncorrected. Analyses by Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y. and Spang Microanalytical Laboratory, Ann Arbor, Mich.

(10) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

(11) The authors wish to express their gratitude to Dr. C. Tamborski of this laboratory for the tri-n-hexylbromosilane used in this work.

reacted ferrocene (3.9 g.; 11% of the original amount). Distillation of the ferrocene-free residue gave III (34.7 g.; 32% yield) which was collected as an orange-red oil within the temperature range of 180–198° (0.17–0.25 mm.). This material was subsequently column-chromatographed on 1000 g. of Woelm, nonalkaline, Grade I alumina. The product, III, was eluted from the column with a benzene-ethanol mixture (35 parts of benzene and 1 part of ethanol) after the column was developed with benzene. The material was chromatographically homogeneous; n_D^{25} 1.5202.

Anal. Calcd. for $C_{28}H_{48}FeSi$: C, 71.76; H, 10.32; Fe, 11.92. Found: C, 71.96; H, 10.30; Fe, 11.85.

The residue obtained from the distillation of the crude reaction product was column-chromatographed on 800 g. of alumina. Development and elution were carried out with benzene, and IV (29.8 g.; 35% yield) was obtained from the eluate. A portion of the product was rechromatographed for analysis; n_D^{25} 1.5054.

Anal. Calcd. for $C_{46}H_{86}FeSi_2$: C, 73.55; H, 11.54; Fe, 7.43. Found: C, 73.23; H, 11.36; Fe, 7.24.

B. III and IV *via* sodiation of ferrocene.[6] Ferrocene (23.3 g.; 0.125 mole), dissolved in toluene, was treated with phenylsodium[12] (0.25 mole) at room temperature during 24 hr.; and at 75–80° for an additional 7 hr. Tri-*n*-hexylbromosilane (90.8 g.; 0.25 mole) was rapidly added (mild exothermic reaction), and the mixture stirred at room temperature overnight; then heated at 70–80° for 24 hr. The reaction mixture, cooled to 10°, was passed through a bed of "Filter-Aid," and the filtrate (500 ml.) was heated on a steam bath *in vacuo* (20 min.) to sublime the unreacted ferrocene (17.9 g.; 77% of the initial amount). The residue was then heated under distillation conditions, and material which was collected up to 100° (0.04 mm.) was not investigated. The undistilled portion (28.2 g. of a dark fluid) was chromatographed on 400 g. of alumina. The chromatogram was developed with cyclohexane and eluted with benzene. Two bright orange-colored bands were successively eluted. The slower-moving band yielded III (580 mg., 0.5% yield) which when rechromatographed was obtained analytically pure; n_D^{25} 1.5202.

Elution of the faster-moving band gave IV (5.63 g., 8% yield); n_D^{25} 1.5054.

C. IV *via* tri-*n*-hexylsilylcyclopentadiene (X). Freshly distilled cyclopentadiene (13.7 g.; 0.21 mole) was added to sodium shot (2.34 g.; 0.10 mole) over a 15-min. period. Evolvement of hydrogen ceased 45 min. after the addition was completed. The reaction mixture was cooled to 5°, and tri-*n*-hexylbromosilane (36.5 g.; 0.10 mole), dissolved in 20 ml. of THF was added with stirring during a 1-hr. period. The mixture was allowed to reach room temperature while the stirring was continued for an additional 2 hr. After the reaction mixture was subsequently heated under reflux during 24 hr., it was cooled to room temperature and passed through a bed of Filter-Aid to remove the white precipitate (NaBr) which was present. The filtrate was evaporated on a steam bath *in vacuo*, and the residue distilled.

Infrared analysis of a fraction collected at 140–160° (0.5–0.7 mm.), n_D^{25} 1.4750–1.4743, indicated the presence of a substituted cyclopentadiene compound. A portion of this material (3.5 g.; 0.01 mole based on the presence of pure X) was dissolved in benzene and treated with *n*-butyllithium (9 ml. of a 0.18*M* ethereal solution), and then heated under reflux during 1 hr. Iron(II) chloride (3.5 g.; 0.02 mole) was added as a slurry in THF, and the reaction mixture heated under reflux for 3 hr.; then stirred at room temperature during an additional 24 hr. After the mixture was poured onto 200 ml. of water–crushed ice and phase-separated, ether extracts of the aqueous phase were combined with the bulk organic portion. The presence of the ferrocene nucleus in this solution was indicated by means of a paper chromatography test.[13] Evaporation of the solvent yielded a dark fluid which was heated to 250° (0.1 mm.) until no further distillate was obtained. The undistilled portion was chromatographed on 30 g. of alumina, and the compound, IV (56 mg., 4% yield), n_D^{25} 1.5056, was obtained from the benzene eluate.

The infrared spectrum of the product was found to be identical to those of the disubstituted compounds (both IV) prepared *via* the 2 metalation procedures.

Acknowledgment. The authors wish to express their appreciation to Mr. F. F. Bentley and associates of this laboratory for the infrared spectra cited in this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

The Active 12-Methyloctadecanoic Acids

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The (+)- and (−)-12-methyloctadecanoic acids have been prepared from (+)- and (−)-2-octanols by the procedure pioneered by Prout, Cason, and Ingersoll.[2] The active acids have higher melting points than the DL-acid.

The preparation of the active 12-methyloctadecanoic acids represents an extension of earlier work[2,3] and the scheme is given in the chart.

The (+)- and (−)-2-octanols[4] (I) were converted to the antipodally pure (−)- and (+)-3-methylnonanoic acids (V) by a four-step procedure in which optical purity was assured by fractional crystallization of the (−)- and (+)-2-octylmalonic acids (IV). The active forms of IV (m.p. 106–108°) were obtained readily by crystallization from hexane; however, the DL-form (m.p. 80–82°) did

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[1] This work was abstracted from the Master of Science theses submitted to the faculty at De Paul University by Donald E. Dickson (1952) and Robert J. Klimkowski (1958).

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