69.5°, reported[17] m.p. 67.5°; *p*-chloroazobenzene, m.p. 88–89°, reported[17] m.p., 87.5°; *p*-bromoazobenzene, m.p. 88–90°, reported[17] m.p. 89°; *p*-iodoazobenzene, m.p. 105–107°, reported[18] m.p. 105°; *p*-methylazobenzene, m.p. 69–71°, reported[19] m.p. 71–72°; *p*-phenylazobenzene, m.p. 154–155°, reported[20] m.p. 150°, and *m*-trifluoromethylazobenzene, m.p. 38–39°, reported[21] m.p., 37°.

The azobenzenes prepared from aniline and the appropriate substituted nitrosobenzenes were: *p*-nitroazobenzene, m.p. 132–134°, reported[11] m.p. 134–135°; *m*-trifluoromethylazobenzene, m.p. 38–39°; and *o*-chloroazobenzene, m.p. 29–31°.

Anal. Calcd. for $C_{12}H_9N_2Cl$: C, 66.52; H, 4.19. Found: C, 66.60, 66.79; H, 4.28, 4.17.

Ferrocenylazobenzenes. The ferrocenylazobenzenes were prepared by the same methods as the azobenzenes, using in each case the aminophenylferrocene and a 10% excess of the appropriate nitroso compound. Their properties and analyses are listed in Table I. The ferrocenylazobenzenes dissolve in alcohol to give colored solutions varying from orange to reddish purple. They are soluble in concd. hydrochloric acid to form red solutions.

p-Ferrocenylazobenzene was also prepared directly from ferrocene and *p*-aminoazobenzene. A solution of 9.3 g. (0.05 mole) of ferrocene was prepared in 27 ml. of concd. sulfuric acid, to yield the ferrocinium ion, and this solution was poured on crushed ice. To this solution was added a solution of diazotized *p*-aminoazobenzene in acetic acid, prepared from 9.9 g. (0.05 mole) of *p*-aminoazobenzene in acetic acid with sulfuric acid and a 10% excess of sodium nitrite at −3°. The mixture was brought to room temperature with stirring overnight. Work-up involved chromatography on alumina (benzene). *p*-Ferrocenylazobenzene was obtained in 21% yield, based on recovery of 38% of the ferrocene. The infrared spectrum of this product was identical with that prepared from *p*-aminophenylferrocene; a mixed melting point showed no depression.

Several nitroso compounds failed to couple with the aminophenylferrocenes. *p*-Nitroso-*N*,*N*-dimethylaniline, *p*-nitrosoanisole, and *m*-nitrosotoluene yielded with the amino compounds intractable tars.

Attempts to diazotize *m*-aminophenylferrocene and *p*-aminophenylferrocene and to couple with *N*,*N*-dimethylaniline failed. In both cases it is doubtful that the diazonium salt was obtained. This is not surprising in view of the report of failures by Nesmeyanov[22] to diazotize *p*-aminophenylferrocene.

Spectra. The spectra were obtained with a Cary Model 14 instrument. The solutions were prepared in absolute alcohol in about $10^{-5}M$ for the ultraviolet spectra and about $10^{-4}M$ for the visible spectra and were allowed to stand overnight in the dark to assure the *trans* form of the azo compounds. Although attempts to detect *cis* and *trans* isomers of the ferrocenylazobenzenes by chromatography on alumina gave no evidence of these two types of isomers, it was deemed desirable to allow these solutions to stand in the dark overnight in view of reports of changes in the spectra of azobenzenes upon exposure to light.[23,24] In view of experience the authors have had with decomposition of solutions of acetylferrocene and other derivatives of ferrocene on standing in acetonitrile, the ferrocenylazobenzene solutions were examined for decomposition on standing. No changes were observed in either the absorption maxima or the extinction coefficients of these solutions over a period of several days.

Acknowledgment. The authors would like to thank the University of North Carolina Research Council for financial assistance with some of the analyses.

CHAPEL HILL, N. C.

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(19) C. Mills, *J. Chem. Soc.*, **67**, 925 (1895).

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(21) V. P. Chernetskii, L. M. Vagupolskii, and S. B. Serebryanyi, *Zhur. Obshcheĭ Khim.*, **25**, 2161 (1955); *Chem. Abstr.*, **50**, 8661 (1956).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Alkali Catalyzed Aldol Condensation of Bisacetylferrocene with Benzaldehyde to Form Mono- and Dibenzaldehyde Derivatives[1]

T. ARTHUR MASHBURN, JR., CHARLES E. CAIN,[2] AND CHARLES R. HAUSER

Received April 4, 1960

Treatment of mixtures of bisacetylferrocene and benzaldehyde with 5% aqueous-ethanolic sodium hydroxide produced a yellow product and a red product, which were evidently mono- and dibenzaldehyde derivatives respectively. The structure of the red product was established as the dibenzal derivative of bisacetylferrocene but that of the yellow product was not determined. Some evidence was obtained that the latter compound had a cyclic vinyl ether structure.

It has previously been shown[3] that acetylferrocene (I) and benzaldehyde undergo the alkali catalyzed aldol type of condensation accompanied by the elimination of water to form the benzal derivative II.

It therefore seemed possible that bisacetylferrocene (III)[4] and benzaldehyde would undergo this

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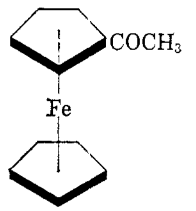
[1] Supported in part by the Office of Ordnance Research, U. S. Army.

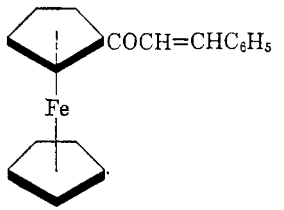
[2] Esso Research and Engineering Company Fellow, 1957–1958.

[3] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

[4] We are indebted to Dr. R. L. Pruett, Union Carbide Chemicals Company, South Charleston, W. Va., for a generous sample of this compound.

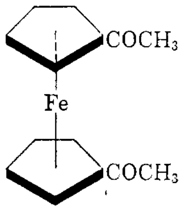


I

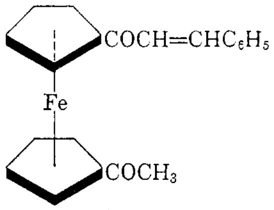


II

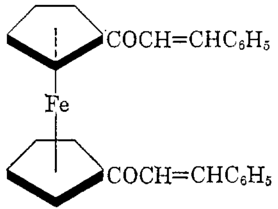
type of condensation to give the mono- and dibenzal derivatives IV and V respectively.



III



IV



V

Actually treatment of mixtures of diketone III and benzaldehyde with 5% aqueous-ethanolic sodium hydroxide produced a yellow product and a red product, the analyses of which were satisfactory for mono- and dibenzaldehyde derivatives, respectively. As might be expected on this basis, the proportion of the yellow product decreased and that of the red product increased as the number of molecular equivalents of benzaldehyde were increased (Table I).

TABLE I

YIELDS OF YELLOW AND RED PRODUCTS FROM BISACETYLFERROCENE (III) WITH VARIOUS EQUIVALENTS OF BENZALDEHYDE

C_6H_5CHO Equiv.	Yellow Prod., Yield, %[a]	Red Prod. (V) Yield, %
1	66–68	6–13
2	60	23
4	22	72
6	5	75

[a] Calculated as a monobenzaldehyde derivative.

Evidence was obtained that the red product was indeed the dibenzal derivative V but that the yellow product was an isomer or a polymer of structure IV. In Table II are summarized some significant bands of the infrared absorption spectra of the red and yellow products and of certain related compounds.

TABLE II

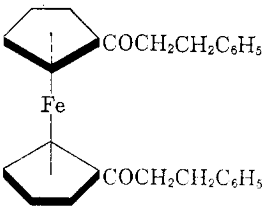
INFRARED ABSORPTION SPECTRA OF THE RED AND YELLOW PRODUCTS AND RELATED COMPOUNDS (μ)

Red Product V[a]	Benzal Derivative II[a]	Benzalacetophenone[b]	Saturated Ketone VI[c]	Saturated Ketone VII[c]	Yellow Product[a]
—	—	—	—	—	3.24
6.03	6.03	6.0	5.87	5.88	6.00
6.23	6.23	6.2	—	—	—
—	—	—	6.77	6.79	—
—	—	—	7.15	7.15	—
7.75	7.75	7.6	7.65	7.64	7.80
—	—	—	—	—	8.05
—	9.0	—	—	8.95	—
—	9.98	—	—	9.90	—
10.20	10.20	10.30	10.09	10.11	10.10
—	—	—	11.27	11.36	11.24
14.3, 14.6	14.1, 14.6	13.5, 14.5	—	—	14.16

[a] Infrared spectrum determined in potassium bromide pellet. [b] Ref. 5. [c] Infrared spectrum determined in carbon tetrachloride solution.

It can be seen from Table II that the infrared spectrum of the red product was almost identical with that of the benzal derivative of monoacetylferrocene (II) and similar to that of benzalacetophenone,[5] both of which are structurally analogous to V. All three compounds showed bands at 6.2 μ and at about 14 μ, which may be ascribed to the conjugated carbon-carbon double bond[6] and to the monosubstituted benzene ring[7] respectively. The 9–10 μ bands exhibited by II but not by the red product (or benzalacetophenone) are attributed[8] to the unsubstituted cyclopentadienyl ring of II.

Further support that the red product had structure V was obtained by its molecular weight and by hydrogenation of the carbon-carbon double bond over palladium-charcoal, about 1.5 molecular equivalents of hydrogen being absorbed. The product was presumably the saturated ketone VI (51%), since its infrared spectrum showed carbonyl absorption at 5.88 μ and no band in the region of 6.2 μ for a carbon-carbon double bond conjugated with the carbonyl group (see Table II).



VI

As a model for such a hydrogenation, benzal derivative II was treated similarly, approximately one molecular equivalent of hydrogen being absorbed. The resulting saturated ketone VII (89%)

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(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, 1958, p. 89.

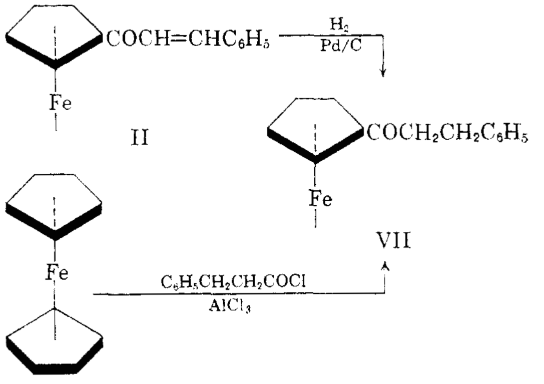
(6) See ref. 5, p. 136.

(7) See ref. 5, p. 76.

(8) See P. L. Pauson, *Quart. Revs.* (*London*), 9, 391 (1955).

was independently synthesized from ferrocene and hydrocinnamoyl chloride (Scheme A).

Scheme A

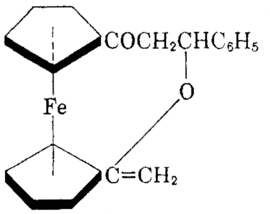


The infrared spectra of the two saturated ketones were almost identical, except for the usual absence of the 9–10 μ bands in the spectrum of VI[8] (see Table II). As these spectra were determined in carbon tetrachloride solution, the phenyl absorption was obscured by the solvent. The spectrum of ketone VII was also determined in a potassium bromide pellet, in which strong phenyl absorption was observed in the 14 μ region. These results are considered to establish the structure of the red product as V.

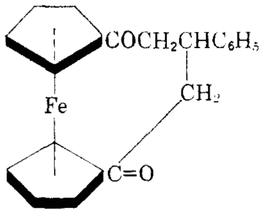
Incidentally, the method of preparation of benzal derivative II from monoacetylferrocene (I) and benzaldehyde was improved to give II in yields of 94–96% instead of the 65–69% yields reported earlier.[3]

It can further be seen from Table II that the infrared spectrum of the yellow product was not consistent with structure IV. Thus, although a carbonyl band was shown at 6.0 μ, no band was observed in the region of 6.2 μ for a conjugated carbon-carbon double bond. Instead, several bands appeared that were not exhibited by the α,β-unsaturated carbonyl compounds. As the analysis of the yellow compound called for a monobenzaldehyde derivative, an isomer or polymer of IV is suggested. A conceivable isomer would be VIII or IX, which might have arisen through intramolecular conjugate addition involving the oxygen or carbon resonance forms of the intermediate anion respectively. A conceivable dimer would be X or XI, which might have arisen through intermolecular conjugate addition of the two resonance forms of the anion.

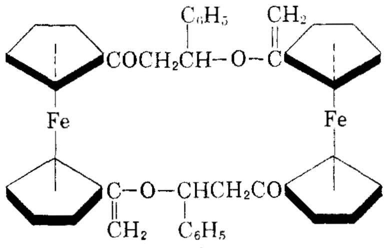
As VIII and IX may correspond to an eight- or nine-membered ring and X and XI to a 16- to 18-membered ring, the latter might appear more likely even though an intermolecular condensation would first be required. Of course all the cyclizations would require the *cis*-configuration (*i.e.*, with the two groups on the same side) which appears to be the normal configuration of at least certain ferrocene derivatives.[9] Even if some ferrocene compounds were normally in the *trans*-configuration, there seems to be free rotation around the iron in solution at normal temperatures.[10,11]



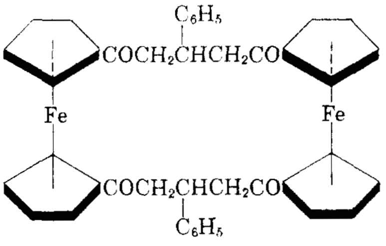
VIII



IX



X



XI

Because the yellow product had a relatively high melting point (>300°) and a relatively low solubility in such solvents as refluxing ethanol, benzene, carbon tetrachloride, tetrahydrofuran, and dimethylformamide, a dimer or even a higher polymer was indicated. Unfortunately, attempts to determine the molecular weight of the yellow product were unsatisfactory because of its insolubility in the usual cryoscopic and ebullioscopic solvents.

Although the structure of the yellow product was not established, its infrared spectra appeared to indicate the presence of a large ring ether group as in VIII and X but not in IX and XI (see Table II). Thus, the product showed a strong band at 8.05 μ, which corresponds to bands in the region of 7.87–8.1 μ reported for this type of group.[12] Moreover, the product gave weak bands at 3.24 μ and 11.24 μ, which seem attributable to the α,α-disubstituted ethylenic linkage found in VIII and X, as bands in these regions among others have been observed for compounds having such a group.[13] While the former band might also have been due to carbon-

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[9] See D. A. Semenov and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 2741 (1957).

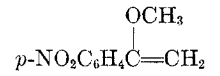
[10] See M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

[11] Yu T. Struchkov, *Zhur. Obshchei Khim.*, **27**, 2039 (1957).

[12] See ref. 5, page 114.

[13] See ref. 5, page 51.

hydrogen stretching in the ferrocene nucleus,[8] the nonferrocene type of vinyl ether XII[14] likewise showed a band at 3.23 μ (and at 3.55 μ) for the methylene double bond group. The band for the vinyl ether group in XII appeared at 9.0 μ, but this shift in value might be attributable to the presence of the nitro group.



$$p\text{-}NO_2C_6H_4\overset{OCH_3}{C}{=}CH_2$$

XII

Indirect evidence was obtained that the yellow product had only one ketone group per ferrocene nucleus in agreement with structures VIII and X. Thus, the product gave a monophenylhydrazone and a mono-2,4-dinitrophenylhydrazone on treatment with large excesses of phenylhydrazine and 2,4-dinitrophenylhydrazine respectively. No diphenylhydrazone or di-2,4-dinitrophenylhydrazone was found.

It should be mentioned that when a suspension of the yellow product in glacial acetic acid containing 5% hydrochloric acid was heated at reflux temperature for two hours under dry nitrogen, decomposition occurred. However, no pure compound was isolated.

EXPERIMENTAL[15]

Condensation of bisacetylferrocene (III) *with benzaldehyde.* This condensation was effected with various molecular equivalents of benzaldehyde by means of dilute aqueous-ethanolic sodium hydroxide to form yellow and red products, the yields of which are summarized in Table I. Experiments are described below employing 1 and 6 equivalents of the aldehyde.

(*A*) *With one equivalent of benzaldehyde. Preparation of yellow product.* To a stirred solution of 1.6 g. (0.04 mole) of sodium hydroxide in 10 ml. of water and 125 ml. of 95% ethanol was added 10.8 g. (0.04 mole) of bisacetylferrocene (III). As soon as the diketone had dissolved, a cold water bath (approximately 15°) was placed around the flask, and 4.2 g. (0.04 mole) of freshly distilled benzaldehyde was slowly added to the solution. The resulting deep red solution was stirred for 90 min., during which time a pink precipitate formed. Stirring was stopped and the solution was allowed to stand overnight in the refrigerator. The pink-yellow solid was collected and washed with water until the washings were neutral to litmus. Recrystallization from ethanol-benzene gave 9.6 g. (66%) of the yellow compound as golden feathers, m.p. >300°, the analysis of which was satisfactory for a monobenzaldehyde derivative of bisacetylferrocene.

Anal. Calcd. for $C_{21}H_{18}O_2Fe$: C, 70.41; H, 5.06; Fe, 15.53 Found: C, 70.38; H, 5.11; Fe, 15.74.

Concentration of the filtrate precipitated 1.0 g. (6%) of the bis-α,β-unsaturated ketone V as small, red crystals, m.p. 206–209°.

(*B*) *With six equivalents of benzoldehyde. Preparation of bis-α,β-unsaturated ketone* V. To a stirred solution of 6 g. (0.150 mole) of sodium hydroxide in 75 ml. of water and 100 ml. of 95% ethanol was added 5.4 g. (0.02 mole) of bisacetylferrocene (III) in 50 ml. of 95% ethanol, followed by 11.5 g. (0.12 mole) of freshly distilled benzaldehyde. The resulting deep red solution was stirred for 6 hr. During this time a very flocculant, red precipitate formed. The stirring was stopped, and the solution was allowed to stand overnight in the refrigerator. The red precipitate was collected and washed with water until the washings were neutral to litmus. The red powder, on recrystallization from ethanol-water, gave 6.7 g. (75%) of the bis-α,β-unsaturated ketone V as red needles, m.p. 208–210°.

Anal. Calcd. for $C_{28}H_{22}O_2Fe$: C, 75.34; H, 4.94; Fe, 12.51. Found: C, 75.06; H, 4.99; Fe, 13.34. *Mol. wt.*[16] Calcd. 446.3. Found: 462.

In addition, there was isolated a very small quantity (approximately 0.3 g.) of the yellow product, m.p. >300°. Mixed melting points and infrared spectra showed these two products to be identical with those isolated under (A).

Hydrogenation of bis-α,β-unsaturated ketone V. To a deep red solution of 1 g. of the unsaturated ketone V in 225 ml. of absolute ethanol was added 400 mg. of 5% palladium on charcoal. The resulting, rapidly stirred mixture was saturated with hydrogen at room temperature (approximately 28°) and atmospheric pressure. After 4 hr. the uptake of hydrogen, having reached approximately 75% of the theoretical, ceased and the reaction was stopped. The mixture was filtered and the filtrate was concentrated to yield a crude red-orange powder. This powder was recrystallized four times from ethanol to give 0.5 g. (51%) of the reduced ketone, presumably, VI, as red-orange needles, m.p. 130–130.5°.

Anal. Calcd. for $C_{28}H_{26}O_2Fe$: C, 74.5; H, 6.04; Fe, 12.4. Found: C, 73.90; H, 5.95; Fe, 12.02.

Hydrogenation of benzalacetoferrocene (II) *to form saturated ketone* VII. The benzal derivative II was prepared by a modification of the earlier procedure.[3]

To a stirred solution of 2.18 g. (0.055 mole) of sodium hydroxide in 20 ml. of water and 10 ml. of 95% ethanol at 30° was added a mixture of 9.8 g. (0.043 mole) monoacetylferrocene and 4.9 g. (0.048 mole) of freshly distilled benzaldehyde in 25 ml. of 95% ethanol. This mixture was stirred for about 10 min. The resulting thick mixture was allowed to stand for 1.5 hr., filtered, and the solid washed with water until the washings were neutral to litmus. The solid was recrystallized from 95% ethanol to give 13.0 g. (96%) of benzalacetoferrocene (II) as red crystals, m.p. 137–139°. Mixed melting points and infrared spectra showed this sample to be identical with an authentic one.

To the deep red solution of 1 g. of unsaturated ketone II in 150 ml. of absolute ethanol was added 500 mg. of 5% palladium on charcoal. The resulting, rapidly stirred mixture was saturated with hydrogen at 30° and atmospheric pressure. After 3 hr. the uptake of hydrogen, having reached approximately 100% of theory, ceased. The mixture was filtered, and the filtrate was concentrated to precipitate 0.88 g. (89%) of the saturated ketone VII as dark red needles, m.p. 85–85.5°. Recrystallization from *n*-hexane failed to raise the melting point.

Anal. Calcd. for $C_{19}H_{18}OFe$: C, 71.6; H, 5.7; Fe, 17.5. Found: C, 71.53; H, 5.35; Fe, 16.7.

Independent synthesis of saturated ketone VII. To a rapidly stirred, cooled solution of 10 g. (0.054 mole) of ferrocene and 9.04 g. (0.054 mole) of hydrocinnamoyl chloride in 200 ml. of anhydrous ethylene chloride was added 15.7 g. (0.108 mole) of anhydrous aluminum chloride at such a rate that the temperature did not rise above 8°. The resulting deep purple solution was stirred at 0° for one-half hour and then refluxed for 4 hr. Ice and excess hydrochloric acid were added, and the two layers were separated. The aqueous layer was extracted twice with small portions of methylene

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(14) We are indebted to Dr. Frank G. Young of Union Carbide Chemicals Co., South Charleston, W. Va., for the infrared spectrum of this compound.

(15) Analyses are by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 21 Spectrophotometer.

(16) Determined using Cottrill boiling point apparatus.

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 byproduct, 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

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[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.