Organometallic π-Complexes. VII. Studies on Mercuriferrocenes[1]

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Treatment of 1,1'-dichloromercuriferrocene with either ethanolic sodium iodide or aqueous sodium thiosulfate solution produces products of the elemental composition $(C_{10}H_8FeHg)_x$. The reactions of these materials with either *n*-butyllithium, followed by carbonation and hydrolysis, or iodine yield ferrocene-1,1'-dicarboxylic acid and 1,1'-diiodoferrocene as the major products, respectively, together with lesser amounts of monosubstituted ferrocenes and ferrocene. The infrared, nuclear magnetic resonance, and mass spectra of $(C_{10}H_8FeHg)_x$ and of diferrocenylmercury are reported and discussed. The spectral data and chemical reactivity of the new mercuriferrocenes are consistent with the general structural formulation involving units of ferrocene bridged by atoms of mercury in a heteroannular arrangement.

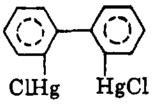
The equilibrium between dialkyl- or diarylmercury compounds, mercuric halides, and organomercuric halides has long been recognized in organomercury chemistry.[3] A recent investigation of this equilibrium by means of proton nuclear magnetic resonance has

$$R_2Hg + HgX_2 \rightleftharpoons 2\ RHgX$$

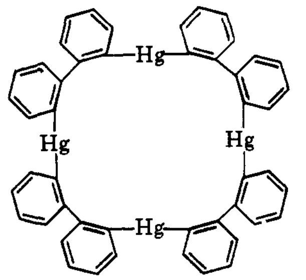
shown that when the organic moiety is methyl or benzyl (and presumably other groups as well) the corresponding organomercuric halide is greatly favored.[4] The formation of organomercuric halides under these conditions has been of appreciable synthetic utility in preparing compounds of the type RHgX.

In the presence of certain reagents which can function as reducing agents or can form complexes with mercuric halides, the equilibrium can be shifted so as to favor the formation of the dialkyl- or diarylmercury compound.[3] Suitable reagents include sodium metal, sodium stannite, sodium iodide, sodium thiosulfate, etc. The synthesis of many compounds of the type R_2Hg from corresponding organomercuric halides has been achieved in this manner.

Several reports have appeared in the literature concerning the application of these procedures to difunctional organomercuric halides. Sawatzky and Wright[5] found that treatment of 1,6-dichloromercurihexane and 1,4-dichloromercuributane with alkaline sodium stannite solution produced mercuracycloheptane and 1,6-dimercuracyclododecane, respectively. Wittig and Herwig[6] have noted that treatment of 2,2'-dichloromercuribiphenyl (I) with ethanolic sodium iodide solution results in the formation of *o*-biphenylenemercury, and later work[7] has indicated that this organomercury compound exists as a cyclic tetramer (II).

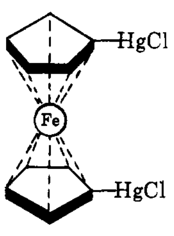


I

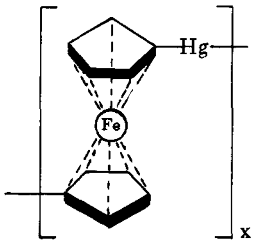


II

Since 1,1'-dichloromercuriferrocene (III) is readily obtained by the mercuration of ferrocene,[8,9] it was of interest to determine if corresponding mercury-bridged ferrocenes (IV) could be obtained under similar conditions. The preparation of diferrocenylmercury from chloromercuriferrocene previously has been accomplished,[8,9] and the reactions of these mercuriferrocenes have been the subject of a number of additional investigations.[10]



III



IV

Experimental

General.—1,1'-Dichloromercuriferrocene was prepared by the mercuration of ferrocene.[8,9] It was purified by repeated extraction with boiling 1-butanol, followed by similar extraction with boiling methanol, filtration, washing, and drying at 110°. *n*-Butyllithium was prepared according to the procedure of Gilman and Morton.[11] Silver powder was prepared by reduction of silver chloride with dextrose.[12] Sodium iodide, sodium thiosulfate, and iodine were reagent grade products. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory and by the analytical section of this laboratory. Infrared analyses were determined on a Beckman IR-4 spectrophotometer. Room temperature n.m.r. measurements were made on a Varian A-60 spectrometer, and measurements at elevated temperatures were made on a Varian V-4300B spectrometer. All melting points are uncorrected, and the melting points of all mercuriferrocenes were determined in sealed capillaries under nitrogen.

Reaction of 1,1'-Dichloromercuriferrocene with Ethanolic Sodium Iodide.—Finely powdered 1,1'-dichloromercuriferrocene (32.85 g., 0.05 mole) was added with stirring to a hot solution of sodium iodide (75.0 g., 0.5 mole) in 1500 ml. of absolute

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[1] Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 34Q; part VI, *Inorg. Chem.*, **1**, 414 (1962).

[2] Department of Chemistry, University of Massachusetts, Amherst, Mass.

[3] (a) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., Inc., Reinhold Publishing Corp., New York, N. Y., 1921, pp. 38ff, 59ff; (b) E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Edwards Brothers, Inc., Ann Arbor, Mich., 1943, pp. 129ff, 167ff (photo-lithoprint reproduction).

[4] M. D. Rausch and J. R. Van Wazer, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

[5] H. Sawatzky and G. F. Wright, *Can. J. Chem.*, **36**, 1555 (1958).

[6] G. Wittig and W. Herwig, *Ber.*, **88**, 962 (1955).

[7] G. Wittig and G. Lehman, *ibid.*, **90**, 875 (1957).

[8] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **97**, 459 (1954).

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

[10] For a review, see M. D. Rausch, *Can. J. Chem.*, **41**, 1289 (1963).

[11] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 285 (1954).

[12] G. Brauer, "Handbuch der Praparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, Germany, 1954, p. 766.

ethanol. The reaction mixture was stirred at reflux for 6 hr. and then allowed to cool to room temperature. The orange-brown solid, containing a few globules of mercury, was washed repeatedly with hot water, with methanol, and was dried. The material was extracted with 500 ml. of boiling nitrobenzene, separated by filtration from a gray insoluble residue, and the filtrate was allowed to cool to room temperature. Filtration produced 5.60 g. of an orange solid (IV), m.p. *ca.* 275°.[13] A portion of this solid was further purified by nitrobenzene extraction and subsequent cooling. This process yielded a slightly purer product which melted at *ca.* 280° with concomitant decomposition and sublimation of ferrocene.

Anal. Calcd. for $(C_{10}H_8FeHg)_x$: C, 31.23; H, 2.10; Fe, 14.55; Hg, 52.16. Found: C, 31.31; H, 2.06; Fe, 14.27; Hg, 51.50.

Reaction of 1,1′-Dichloromercuriferrocene with Aqueous Sodium Thiosulfate.—Finely powdered 1,1′-dichloromercuriferrocene (6.57 g., 0.01 mole) was added to 100 ml. of a concentrated aqueous solution of sodium thiosulfate and the suspension was stirred at room temperature for 16 hr. The insoluble material was collected by filtration, washed repeatedly with hot water and with methanol, and was dried. The residue was extracted several times with hot benzene until the extracts were nearly colorless, and was subsequently extracted with 200 ml. of boiling nitrobenzene. After the extracts had been cooled sightly, 200 ml. of *n*-heptane was added and the mixture allowed to cool to room temperature. The orange-brown product IV which had separated was collected by filtration, washed with benzene, and was dried.

Anal. Calcd. for $(C_{10}H_8FeHg)_x$: C, 31.23; H, 2.10; Fe, 14.55; Hg, 52.16. Found: C, 31.21; H, 2.00; Fe, 14.54; Hg, 51.93

The product did not possess a definite melting point; it slowly decomposed with sublimation of ferrocene on heating over 300°.

Reaction of IV with Iodine.—A solution of iodine (12.7 g., 0.05 mole) in 50 ml. of xylene was warmed to 60° and was slowly added with stirring to a suspension of IV in 300 ml. of xylene. During the addition the reaction mixture was maintained at *ca.* 75°. The reaction mixture was maintained at 70–75° for an additional 0.5 hr. and then allowed to cool overnight to room temperature.

The black crystalline residue was collected by filtration, dried in the filter funnel, and was stirred for 1.5 hr. with 100 ml. of a 10% sodium thiosulfate solution. This process was repeated and the resulting gummy black residue was extracted with ethyl ether until the extracts were colorless. The ether extracts were washed with water and were dried over anhydrous sodium sulfate.

The solvent was evaporated and the resulting orange oil was dissolved in a minimum amount of hexane. The hexane solution was chromatographed on a 2.0 by 61 cm. column of Merck activated alumina. Elution with hexane developed three distinct yellow bands. The first band produced *ca.* 5 mg. of ferrocene, m.p. 172–173°. The second band produced 0.03 g. of iodoferrocene, m.p. 47.5–48°. A mixture melting point determination with an authentic sample of iodoferrocene was undepressed, and the infrared spectra of the two samples (potassium bromide pellets) were identical. The proton n.m.r. spectrum [10% (wt. to vol.) in deuteriochloroform] of the product exhibited two apparent triplets and a sharp singlet (intensity ratio, 2:2:5) at 5.67, 5.92, and 5.88 τ, respectively, and is in agreement with the proposed structure.

Continued elution with hexane produced a third band, although it was noted that this product had partly decomposed on the column. The solvent was evaporated and the product was placed on a rotary evaporator at 0.05 mm. for several hours. There remained 0.18 g. of a viscous orange oil.

Anal. Calcd. for $C_{10}H_8FeI_2$: C, 27.31; H, 1.83. Found: C, 27.65; H, 1.99.

The infrared spectrum of this product (neat) exhibited no absorption bands near 9 or 10 μ, and the proton n.m.r. spectrum [10% (wt. to vol.) in deuteriochloroform] consisted of two apparent triplets of equal intensity at 5.68 and 5.90 τ. The elemental analysis together with the infrared and n.m.r. spectra establish the product at 1,1′-diiodoferrocene. This product previously has been obtained in impure form by the iodination of 1,1′-dichloromercuriferrocene.[14]

Reaction of IV with *n*-Butyllithium.—The reaction was run in a 100 ml. one-necked flask equipped with a nitrogen inlet and a magnetic stirring bar. Under nitrogen and with stirring, 0.016 mole of *n*-butyllithium contained in 20 ml. of ethyl ether was added to a suspension of IV (0.77 g.) in 40 ml. of a 1:1 mixture of ethyl ether and benzene (both solvents had been dried over sodium). The reaction mixture was stirred for 10 min. during which time the solid totally dissolved and the solution turned deep red. The solution was poured onto a mixture of Dry Ice and ethyl ether. After hydrolysis with water the phases were separated, the ether phase was washed twice with water, and the basic aqueous phase and extracts were acidified with dilute hydrochloric acid. The orange precipitate which had formed was collected by filtration, washed with water, and was dried (0.30 g.). A 0.15-g. portion of this crude product was extracted four times with 10-ml. portions of boiling benzene. The last extracts were colorless, indicating complete removal of any ferrocenemonocarboxylic acid. Evaporation of the solvent produced 0.02 g. of crude ferrocenemonocarboxylic acid, m.p. 180–190° dec. The product remaining after benzene extraction did not melt but slowly decomposed on heating over 250°. The infrared spectrum of this material (potassium bromide pellet) was virtually identical to the infrared spectrum of an authentic sample of ferrocene-1,1′-dicarboxylic acid with the exception that very weak absorption bands at 9.03 and 9.98 μ also were present. Recrystallization of this material from glacial acetic acid failed to eliminate these two absorption bands in the infrared spectrum of the resulting product.

The ether phase was dried over anhydrous sodium sulfate, the solvent was evaporated, and the residue was chromatographed on alumina in hexane solution. There was obtained 0.52 g. of di(*n*-butyl)mercury (infrared spectrum identical with that of an authentic sample) and 0.018 g. of ferrocene, m.p. 170–172° (mixture melting point determination with an authentic sample was undepressed).

An additional 0.11-g. portion of the crude acid was esterified by means of methanol containing a drop of sulfuric acid. Chromatography of the reaction products on alumina using benzene as the solvent and eluent produced carbmethoxyferrocene (0.012 g., m.p. 69–70°). A mixture melting point determination of this product with an authentic sample (m.p. 70–71°)[15] was undepressed, and the infrared spectra of the two samples (potassium bromide pellets) were identical. The proton n.m.r. spectrum [10% (wt. to vol.) in deuteriochloroform] of the product exhibited two apparent triplets and two singlets (intensity ratio, 2:2:5:3) at 5.21, 5.63, 5.81, and 6.21 τ, respectively, and is in accordance with the proposed formulation.

Continued elution using mixtures of benzene and chloroform produced 0.086 g. of 1,1′-dicarbmethoxyferrocene. After a recrystallization from aqueous methanol the product melted at 110–111°. A mixture melting point determination of this product with an authentic sample of 1,1′-dicarbmethoxyferrocene (m.p. 113°) was undepressed, and the infrared spectra (potassium bromide pellets) of the two samples were identical. The proton n.m.r. spectrum of this product [10% (wt. to vol.) in deuteriochloroform] exhibited two apparent triplets and a singlet (intensity ratio, 4:4:6) at 5.18, 5.60, and 6.18 τ, respectively, and is in accordance with the proposed formulation.

Thermal Decomposition of IV in the Presence of Silver.—An intimate mixture of IV (2.25 g., prepared by the sodium iodide method) and silver powder (0.058 g.-atom, 6.26 g.) was added under nitrogen to a Schlenk tube modified for sublimation. The tube was heated for 16 hr. in a bath of Wood's metal maintained at *ca.* 300°. The material which had sublimed on to the sides of the tube was collected, extracted with 100 ml. of boiling benzene, separated by filtration from a small amount of metallic mercury, and the filtrate was concentrated to *ca.* 20 ml. and cooled. The crystals which had separated (0.022 g.) were redissolved in 100 ml. of boiling benzene and the clear solution was again concentrated until crystals had begun to form (*ca.* 15 ml.). The orange-red crystals (0.015 g.) obtained in this manner did not melt or decompose when heated in a sealed capillary under nitrogen at temperatures up to 375°.

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[13] In several runs, cooling of the nitrobenzene extracts failed to produce any appreciable amount of product. In these instances the extraction process was repeated.

[14] A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **100**, 1099 (1955).

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

TABLE I

PROTON N.M.R. SPECTRA OF SOME FERROCENYLMERCURY COMPOUNDS

Compound	Chemical shifts, τ, and multiplicity[a,b]	Temp., °C.	Solvent[c]
$C_5H_5FeC_5H_4HgCl$	5.66 (t), 5.55 (s), 5.33 (t)	94	o-$C_6H_4Cl_2$
$C_5H_5FeC_5H_4HgCl$	6.12 (t), 5.94 (s), 5.71 (t)	94	$C_6H_5OC_6H_5$
$(C_5H_5FeC_5H_4)_2Hg$	5.60 (t), 5.37 (s), 5.24 (t)	94	o-$C_6H_4Cl_2$
$(C_5H_5FeC_5H_4)_2Hg$	5.98 (t), 5.82 (s), 5.59 (t)	94	$C_6H_5OC_6H_5$
$(C_5H_5FeC_5H_4)_2Hg$	6.03 (t), 5.90 (s), 5.73 (t)	94	$C_6H_5NO_2$
$(C_5H_4FeC_5H_4Hg)_x$[d]	5.77, 5.50[e]	167	$C_6H_5NO_2$
$(C_5H_4FeC_5H_4Hg)_x$[f]	6.00, 5.73[e]	184	$C_6H_5NO_2$

[a] With tetramethylsilane as an external standard. [b] t = apparent triplet, s = singlet. [c] All spectra were determined as saturated solutions at the stated temperature. [d] Prepared by the sodium iodide method. [e] Peaks were very weak and were not resolved. [f] Prepared by the sodium thiosulfate method.

Anal. Calcd. for $(C_{10}H_8Fe)_x$: C, 65.28; H, 4.38; Fe, 30.35. Found: C, 65.40; H, 4.36; Fe, 30.35.

The product was only very slightly soluble in common organic solvents. The infrared spectrum of this material (potassium bromide pellet) exhibited a very weak absorption band at 9.05 μ and a band of strong intensity at 10.0 μ. Other absorption peaks were noted at 3.23, 7.05, 7.25, 7.90, 9.55, 9.70, 10.95, 11.38, 11.75, 11.95, 12.10, and 12.40 μ.

The filtrate after separation of the orange-red crystals was chromatographed on alumina. Elution with hexane–benzene mixtures removed 0.10 g. of ferrocene, m.p. 171–173°. Continued elution with benzene produced 0.010 g. of biferrocenyl, m.p. 232–235° dec. A mixture melting point determination of this material with an authentic sample of biferrocenyl (m.p. 239–240°)[16] was not depressed, m.p. 232–236°.

The gray reaction residue (7.20 g.) was collected and finely powdered in a mortar. The powdered residue was extracted repeatedly with boiling nitrobenzene, with benzene, and was dried at 110°. Analysis of the residue for carbon, hydrogen, and iron was made, using 50–60-mg. samples in the combustion analysis in order to ensure high accuracy and reproducibility in the hydrogen determination.

Anal. Found: C, 5.35, 5.34; H, 0.36, 0.34; Fe, 2.62.

The g.-atoms of each element were calculated and carbon was assigned a relative value of 10.0. On this basis, the ratio of g.-atoms of carbon–hydrogen–iron was 10.0:7.8:1.0. This ratio closely approximates that required for the presence of polyferrocenylene $(C_{10}H_8Fe)_x$ in the residue.

In another experiment under the same conditions employing 1.16 g. of IV (prepared *via* the sodium iodide method) and 3.24 g. of silver, there was obtained 0.030 g. of ferrocene, 0.005 g. of biferrocenyl, and 0.008 g. of the orange-red crystalline product (m.p. >375°; infrared spectrum identical with the product described previously). Analysis of the reaction residue indicated that the ratio of carbon–hydrogen–iron was 10.0:8.1:1.0. In yet another experiment under these conditions starting with IV that had been prepared by the sodium thiosulfate method, very small amounts of ferrocene and biferrocenyl were isolated, although the high melting orange-red product was not detected. Analysis of the reaction residue after extraction indicated the carbon–hydrogen–iron ratio to be 10.0:7.7:0.9.

Results and Discussion

Treatment of 1,1′-dichloromercuriferrocene with either ethanolic sodium iodide or aqueous sodium thiosulfate solution produced materials which, like the starting compound, were virtually insoluble in most organic solvents examined. By digestion of the reaction products with hot nitrobenzene and subsequent cooling of the extracts, however, orange-brown solids were obtained. Chemical analyses of the products agree well with the formula $(C_{10}H_8FeHg)_x$ (IV). The very limited solubilities of these products in organic solvents have thus far prevented molecular weight determinations under the usual conditions. It was hoped that such determinations could be accomplished by means of ebulliometry in diphenyl ether, as has been reported recently for the molecular weight determination of the very insoluble compound "tetraphenylcubane."[17,18] Subsequent nuclear magnetic resonance (n.m.r.) studies (*vide infra*) have indicated, however, that ferrocene compounds containing carbon–mercury bonds react slowly with proton-containing solvents such as diphenyl ether at elevated temperatures.

The infrared spectra of IV (potassium bromide pellet) prepared by either method are generally similar to the spectrum of diferrocenylmercury. The most notable difference is the marked diminution of the absorption modes near 9 and 10 μ. It is well known that ferrocenes in which both rings are substituted (*i.e.*, there are no unsubstituted cyclopentadienyl rings) uniformly do not exhibit absorption in the 9 and 10-μ regions, while the presence of absorption bands in the spectra of ferrocene derivatives in these regions is frequently indicative of an unsubstituted cyclopentadienyl ring in the molecule.[19,20] The appearance of a very weak absorption band at 9.05 μ and an absorption shoulder at 10.0 μ in the spectrum of IV may thus be due to the presence of small amounts of unsubstituted cyclopentadienyl rings, perhaps as part of ferrocenyl end groups. It should be noted, however, that the infrared spectrum of analytically pure 1,1′-dichloromercuriferrocene likewise exhibits very weak absorption bands at 9.05 and 10.0 μ. The occurrence of very weak bands in the 9 and 10-μ region for mercuriferrocenes III and IV might, therefore, be due to the presence of very small amounts of homoannularly dimercurated ferrocenes. This point is being further investigated.

The proton n.m.r. spectra of both diferrocenylmercury and IV are reported in Table I. At 94° the spectrum of diferrocenylmercury in nitrobenzene, o-dichlorobenzene, or diphenyl ether solution consisted of two apparent triplets and a singlet with area intensities of 2:2:5. The two apparent triplets result from spin–spin coupling of the α- and β-protons in the substituted cyclopentadienyl ring, while the singlet is due to the protons in the unsubstituted cyclopentadienyl ring. These results are in agreement with the structure proposed for diferrocenylmercury, and are consistent with the n.m.r. spectra of many other monosubstituted metallocene derivatives.[21]

Several attempts to observe spin–spin coupling between the α-hydrogens and Hg^{199} ($I = {}^1/_2$, natural

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(16) M. D. Rausch, *J. Am. Chem. Soc.* **82**, 2080 (1960).

(17) H. H. Freedman and D. R. Peterson, *ibid.*, **84**, 2837 (1962).

(18) M. Tsutsui, *Chem. Ind.* (London), 780 (1962).

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

(20) For a recent discussion of this generalization, see E. W. Neuse and D. S. Trifan, *ibid.*, **84**, 1850 (1962).

(21) M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963).

abundance = 16.9%) in diferrocenylmercury, and thus to assist in the assignment of the two apparent triplets, were unsuccessful. Protons that are two carbons removed from an atom of mercury (*e.g.*, in diethylmercury) are known to exhibit strong coupling with Hg^{199},[22,23] although the rigid geometry of the cyclopentadienyl ring apparently does not allow spin–spin coupling of this sort to occur in diferrocenylmercury.

On extended heating in nitrobenzene, *o*-dichlorobenzene, or diphenyl ether at 160–180°, diferrocenylmercury apparently reacted with the solvent. Under these conditions a broad new resonance absorption became superimposed on one of the apparent triplets, and the intensity of this peak increased as a function of time.

Attempts to obtain a proton n.m.r. spectrum of IV were handicapped due to the very limited solubility of these products in organic solvents. Nevertheless, saturated solutions of IV in nitrobenzene were prepared at 160–180°, and n.m.r. spectra were obtained at these temperatures (Table I). The spectra were recorded as rapidly as possible after preparation of the solution in order to minimize decomposition and reaction with the solvent. Although the resonance peaks were weak due to the low solubility of the product even at these temperatures and the peaks were not resolved due to the high radiofrequency signal required for detection, two distinct peaks of approximately equal intensity were observed. This result is in accord with the proposed formulation IV, since such a structure could possess two distinct types of nonequivalent protons.

The mass spectra of diferrocenylmercury and IV were determined with a C. E. C. Type 21–110 mass spectrometer equipped with a spark source and a photographic plate ion detector. Under these conditions, mass ions attributable to the parent compounds or to $FeC_{10}H_9^+$ or $FeC_{10}H_8^+$ fragments could not be detected. On the contrary, the spectra of both compounds were very similar and exhibited moderately intense lines due to $Fe^{56}C_{10}H_{10}^+$ as well as much weaker lines due to $Fe^{54}C_{10}H_{10}^+$. Under the conditions of the spark gap, ferrocenyl and ferrocenylene fragments formed by rupture of carbon–mercury bonds are apparently readily hydrogenated to produce ions of the ferrocene molecule. This facile hydrogenation is consistent with the chemical reactions of mercuriferrocenes described later. Both compounds also produced lines at mass 121 which can be attributed to the $FeC_5H_5^+$ ion. In addition, lines attributable to other hydrocarbon fragments as well as to mercury (seven isotopes) and iron (four isotopes) were noted, indicating decomposition of the parent compounds into basic atomic constituents. Further studies concerning the analysis of these and other organomercury compounds using a gas ion source and low voltage mass spectrometry are in progress.

The reaction of IV with iodine followed by sodium thiosulfate solution produced 1,1′-diiodoferrocene as the principal product, together with lesser amounts of iodoferrocene and ferrocene. Treatment of IV with an excess of *n*-butyllithium followed by carbonation and hydrolysis produced a mixture of ferrocenecarboxylic acids, together with di-(*n*-butyl)mercury and a very small amount of ferrocene. The principal product from this reaction appears to be ferrocene-1,1′-dicarboxylic acid, although the presence of very weak absorption bands near 9 and 10 μ in the spectrum of this product suggests the presence of a small amount of a homoannular diacid. These weak bands were noted even after the crude acid had been repeatedly extracted with boiling benzene (conditions under which ferrocenemonocarboxylic acid is very soluble), or after it had been recrystallized from glacial acetic acid. A lesser amount of ferrocenemonocarboxylic acid was obtained from the benzene extracts. Esterification of the crude acid and subsequent chromatographic separation of the products produced 1,1′-dicarbmethoxyferrocene as the principal product, together with a smaller amount of carbmethoxyferrocene.

The isolation of monosubstituted ferrocenes from the reactions of IV described previously does not necessarily indicate the presence of a $FeC_{10}H_9$–Hg group in the starting product. Diferrocenylmercury is known to produce ferrocene in many reactions as a result of concomitant hydrogenation of the ferrocenyl–mercury bond,[1,24–27] and "symmetrized 1,1′-dichloromercuriferrocene" has been reported to form ferrocene as one of the products when it is allowed to react with cupric chloride.[27] The isolation of very small amounts of ferrocene in the present study from the reaction of IV with iodine and with *n*-butyllithium is further evidence for partial hydrogenation of the ferrocenyl–mercury bond.

The thermal decomposition of diferrocenylmercury in the presence of either palladium black[24] or silver[1] has been shown to yield ferrocene, biferrocenyl, and probably polyferrocenylene. A similar reaction between IV and silver might be expected to produce polyferrocenylene almost exclusively by means of stepwise elimination of mercury. When IV was heated with silver at *ca.* 300° for extended periods, only very small amounts of ferrocene and biferrocenyl could be detected (in contrast to the similar decomposition of diferrocenylmercury). In several experiments an orange-red crystalline product sublimed from the residue in very small amounts. The elemental analysis of this product agreed closely to the composition required for polyferrocenylene, although the very limited solubility of the material precluded a molecular weight determination. Analysis of the reaction residue from several experiments, following extraction of any low molecular weight materials, indicated that the residue contained polyferrocenylene.[28]

The chemical reactions of these products, together with the spectral analyses, support the proposed general formulation IV. It seems most probable that the products obtained by treatment of 1,1′-dichloromer-

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(22) R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

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(26) D. Seyferth, H. P. Hofmann, R. Burton, and J. F. Helling, *Inorg. Chem.*, **1**, 227 (1962).

(27) A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 47 (1962).

(28) Polyferrocenylene also can be produced by the Ullmann reaction of 1,1-diiodoferrocene and copper bronze (M. D. Rausch, unpublished studies).

curiferrocene with either ethanolic sodium iodide or aqueous sodium thiosulfate solution are mixtures of linear polymercuriferrocenylenes possibly containing cyclic polymers. By analogy to other mercury containing ring systems[7,29,30] the value of x is probably very low.

[29] G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 883 (1958).

[30] G. Wittig, E. Hahn, and W. Tochtermann, *ibid.*, **95**, 431 (1962).

Fulvenes and Thermochromic Ethylenes. XXXIII.[1] Polycyclic Derivatives of Heptafulvene

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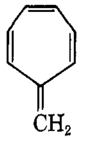
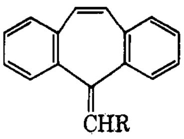
Four polycyclic heptafulvenes (III, IV) have been synthesized, and their spectra and dipole moments have been measured. The data are compared with the theoretical predictions.

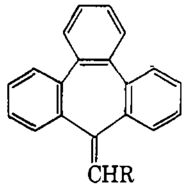
It has been calculated[2a,b] that anellation of benzene rings to the system of heptafulvene (I) will first produce a hypsochromic effect which will change into a bathochromic one upon addition of even more rings. Furthermore, phenyl substitution at the exocyclic carbon atom of I will, on the one hand, increase the polarity of the semicyclic double bond, and, on the other hand, cause a hypsochromic shift. As the experimental results as yet have not borne out the theory,[3] the most complex benzologs of I prepared so far being the 1-methylene-2,3,6,7-dibenzocyclohepta-2,4,6-triene (II) and 1-methylene-2,3,4,5,6,7-tribenzocyclohepta-2,4,6-triene[4] (IIa) type, it seemed of interest to study some higher benzologs and the corresponding heptafulvene ketones.



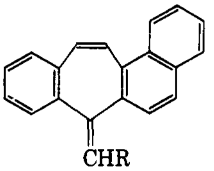
I



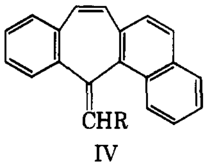
II



IIa

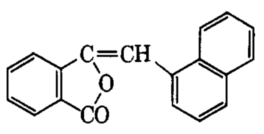


III

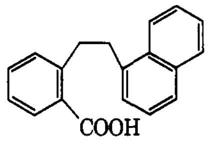


IV

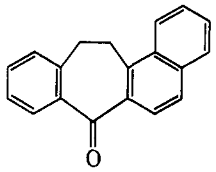
Four heptafulvenes of type III and IV have now been prepared. The synthesis followed the route used[5-7] for the preparation of 2,3,6,7-dibenzocyclohepta-2,4,6-trien-1-one (as II). From phthalic anhydride and 1-naphthylacetic acid, (1-naphthylmethylene)phthalide (V) was obtained. Its reduction with phosphorus and hydriodic acid gave *o*-[β-(1-naphthyl)ethyl]benzoic acid (VI) which was cyclized with polyphosphoric acid to the ketone VII. Successive treatment with bromine and pyridine converted the latter into 8,9-benzo-7-oxo-7*H*-cyclohepta[*a*]naphthalene (VIII). Analogously, the isomeric 9,10-benzo-11-oxo-11*H*-cyclohepta[*a*]naphthalene (IX) was synthesized starting from 2-naphthylacetic acid.



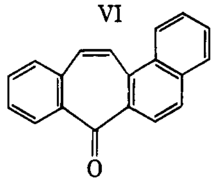
V



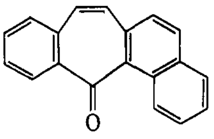
VI



VII



VIII



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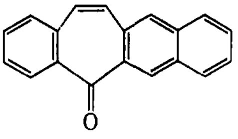
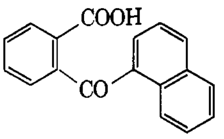
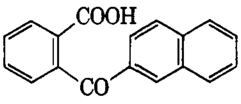


X



XI



XII

In the cyclization of *o*-[β-(2-naphthyl)ethyl]benzoic acid, the H isomer of VI, theoretically IX or X, could be formed, depending on whether the reaction leads from position 2 to 1 or 3 of the naphthalene nucleus. Although the former alternative, and thus IX seemed more likely, an exact proof was considered necessary. Ozonization of the heptafulvene ketone led to a dicarboxylic acid which upon thermal decarboxylation yielded *o*-(1-naphthoyl)benzoic acid (XI), identical with an authentic sample. This is consistent with formula IX; in this sequence of reactions X would have given *o*-(2-naphthoyl)benzoic acid (XII).

It is interesting to note that there is no large difference in the carbonyl frequency (potassium bromide

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[1] Part XXXII: E. D. Bergmann, A. Heller, and H. Weiler-Feilchenfeld, *Bull. soc. chim. France*, 635 (1959).

[2] (a) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, **47**, 484 (1959); (b) E. D. Bergmann, *et al.*, *Bull. soc. chim. France*, **18**, 684 (1951).

[3] See E. D. Bergmann, "Progress of Organic Chemistry," Vol. 3, Butterworths Publications, Ltd., London, 1955, p. 81.

[4] E. D. Bergmann and J. Klein, *J. Org. Chem.*, **23**, 512 (1958).

[5] W. Treibs and H. J. Klinkhammer, *Ber.*, **83**, 367 (1950).

[6] E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim. France*, **18**, 684 (1951).

[7] A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, **53**, 1668 (1951).