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Ferrocene and Related Organometallic π-Complexes. VI. Thermal Decomposition of Diferrocenylmercury[1,2]

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Thermal decomposition of diferrocenylmercury in the presence of silver produces biferrocenyl in yields of 30 to 61%, together with varying amounts of ferrocene and possibly polyferrocenylene. The results indicate a homolytic mechanism of decomposition involving ferrocenyl radicals and ferrocenylene diradicals. Simultaneous decomposition of diferrocenylmercury and other diarylmercury compounds in the presence of silver has provided a new synthesis of arylferrocenes. Reaction of diferrocenylmercury with *n*-butyllithium produces monolithioferrocene.

Biferrocenyl (II) first was isolated by Rausch and co-workers from an anomalous reaction involving lithioferrocene and trialkylchlorosilanes.[3] More recently, Ullmann coupling reactions of haloferrocenes have provided an unequivocal and high-yield synthesis of biferrocenyl.[4–6]

As an alternative synthesis of this compound, we have investigated the reaction of diferrocenylmercury and silver at elevated temperatures. Our studies were prompted by the report that *o*-biphenylenemercury and silver react at 300° with elimination of mercury and formation of biphenylene.[7] During the course of our studies, Nesmeyanova and Perevalova described a reaction between diferrocenylmercury and palladium black.[8] The yield of biferrocenyl by their method, however, was only 1–6%.

Since the very earliest researches in organomercury chemistry, it has been observed that symmetrical diaryl- or diaralkylmercury compounds of the type R_2Hg decompose at elevated temperatures to yield coupling products (R–R) and/or products resulting from hydrogen abstraction (R–H).[9–11] Razuvaev and Koton made an extensive study concerning the thermal decomposition of organomercury compounds under a variety of conditions.[12] They observed that a variety of metals greatly catalyzed the thermal decomposition of diarylmercury compounds, and postulated the intermediate formation of free aryl radicals.

Our initial studies involved the heating of intimate mixtures of diferrocenylmercury and silver powder for 17-hr. periods at varying temperatures. These results are summarized in Table I.

At 100 and 160°, no biferrocenyl could be de-

TABLE I

THERMAL DECOMPOSITION OF DIFERROCENYLMERCURY IN PRESENCE OF SILVER

[Molar ratio of $(C_{10}H_9Fe)_2Hg$:Ag = 1:8; 17 hr.; N_2]

Temp., °C.	$FeC_{10}H_{10}$, % yield[a]	$(FeC_{10}H_9)_2$, % yield[a]
100[b]	3	0
160[b]	3	0
230	68	0
265	29	54
320	29	43
265 (Ag absent)	68	13

[a] Calculated on the basis that one mole of diferrocenylmercury produces one mole of ferrocene or one mole of biferrocenyl. [b] The starting materials were largely recovered.

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[1] Part V: M. D. Rausch, *J. Org. Chem.*, **26**, 3579 (1961).

[2] Presented in part at the 140th National Meeting, American Chemical Society, Division of Organic Chemistry, Sept. 3–8, 1961; see Abstracts of Papers, p. 34-Q.

[3] M. D. Rausch, M. Vogel, H. Rosenberg, D. Mayo, and P. Shaw, Wright Air Development Center Technical Report 57-62, Part II, February, 1958; ASTIA Document No. 150979. This report has been released to the Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C., for sale to the general public.

[4] M. D. Rausch, *J. Am. Chem. Soc.*, **82**, 2080 (1960).

[5] M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

[6] E. G. Perevalova and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **132**, 1093 (1960), recently have reported similar results.

[7] G. Wittig and W. Herwig, *Chem. Ber.*, **87**, 1511 (1954).

[8] O. A. Nesmeyanova and E. G. Perevalova, *Doklady Akad. Nauk S.S.S.R.*, **126**, 1007 (1959).

[9] E. Dreher and R. Otto, *Ann.*, **154**, 93 (1870).

[10] A. N. Nesmeyanov, *Uspekhi Khim.*, **3**, 34 (1934).

[11] Unsymmetrical organomercury compounds of the type R–Hg–R′ are particularly unstable to heat, decomposing into symmetrical compounds R_2Hg and R'_2Hg [M. S. Kharasch and R. E. Marker, *J. Am. Chem. Soc.*, **48**, 3130 (1926)].

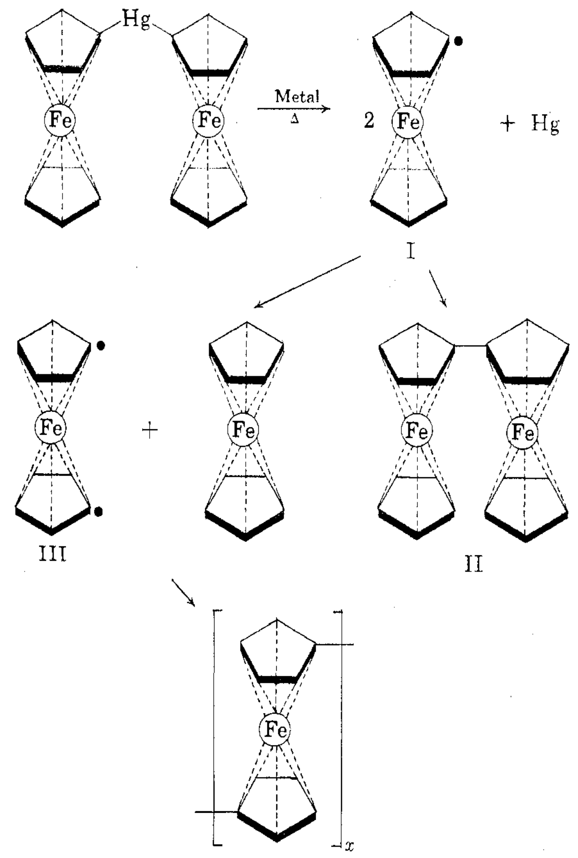
[12] G. A. Razuvaev and M. M. Koton, *J. Gen. Chem. U.S.S.R.*, **1**, 864 (1931); **4**, 647 (1934); **5**, 361 (1935); *Ber.*, **66B**, 854 (1933); **66B**, 1210 (1933).

tected, and ferrocene was isolated in *ca.* 3% yield. Thermal decomposition of diferrocenylmercury in the presence of silver at 230° was very pronounced; ferrocene was formed in 68% yield, but once again no biferrocenyl could be detected. At 265°, both ferrocene and biferrocenyl were formed in yields of 29 and 54%, respectively. Higher reaction temperatures did not greatly change the product ratio. In a number of other experiments involving reaction temperatures between 230 and 290° and reaction times from 3 to 52 hr., the yield of biferrocenyl varied from 30 to 61%.

The data indicate that when silver is used as the catalyst, reaction temperatures greater than the melting or decomposition point of diferrocenylmercury (*ca.* 233–236°) must be employed in order to promote the dimerization reaction to any significant extent. The marked catalytic effect of silver in promoting dimerization to biferrocenyl was illustrated by heating diferrocenylmercury alone at 265° for a 17-hr. period. Ferrocene was formed in 68% yield, while the yield of biferrocenyl dropped to 13%.

The nature of the catalytic effect of metals such as silver on the thermal decomposition of diarylmercury compounds is not yet fully understood. It seems quite probable, however, that the mechanism of decomposition of diferrocenylmercury in the presence of silver parallels that proposed by Nesmeyanova and Perevalova in their studies, *i.e.*, formation of mercury and intermediate ferrocenyl radicals (I) *via* homolytic scission of the carbon–mercury bond. Ferrocenyl radicals thus formed could either couple to yield biferrocenyl (II), or abstract hydrogen to form ferrocene and ferrocenylene diradicals (III) (assuming the species being hydrogen-abstracted is another ferrocenyl radical). Resulting ferrocenylene diradicals apparently unite to form a polymer, since no biferrocenylene could be detected in any of our studies. Analysis of the reaction residue for its carbon, hydrogen, and iron content, following extraction of any low molecular weight materials, indicates the presence of polyferrocenylene.

No examples of the formation of unsymmetrical biaryls by thermal, catalytic decomposition of mixed diarylmercury compounds have been reported in the literature. It seems reasonable to assume that if such decompositions proceed by an essentially homolytic mechanism, mixed biaryls might be expected to be formed. In the ferrocene series, this could lead to a new synthetic route for arylferrocenes.[13]



Reactions involving the thermal decomposition of equimolar amounts of diferrocenylmercury and diphenylmercury in the presence of excess silver produced phenylferrocene in 45% yield, together with lesser amounts of biferrocenyl, biphenyl, and ferrocene. The mixture of products could be separated by chromatography on alumina. The reaction of diferrocenylmercury with other diarylmercury compounds was extended for the preparation of the isomeric 2-, 3-, and 4-biphenylylferrocenes. These results are tabulated in Table II. 4-Biphenylylferrocene also was synthesized by reaction of 4-biphenylyldiazonium chloride and ferrocene, and was shown to be identical to the product isolated from the decomposition reaction.

Gilman and co-workers[14] have shown that

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(13) Arylferrocenes previously have been prepared by reaction of arylcyclopentadienyl–metal compounds with iron(III) chloride [P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954)]; by reaction of aryldiazonium salts with ferrocene [G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955); V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3012 (1955); A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954)]; and by Ullmann coupling of iodoferrocene and 1-iodo-2-nitrobenzene.[4,5]

(14) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **63**, 1443 (1941); H. Gilman, F. W. Moore, and R. G. Jones, *ibid.*, **63**, 2482 (1941).

TABLE II

FORMATION OF ARYLFERROCENES

[Molar ratio of $(FeC_{10}H_9)_2Hg:Ar_2Hg:Ag$ = 1:1:15; 235-300°; 17-22 hr.]

Compound	M.p., °C.	Yield, %	Found C	Found H	Found Fe	Found Mol. wt.
Phenylferrocene	111–112	45	...	...	...	...
2-Biphenylylferrocene[a]	133–134	6	77.86	5.59	16.65	324
3-Biphenylylferrocene[a,b]	102.5–103	22	76.91	5.45	17.01	322
4-Biphenylylferrocene[a]	164–165	20	78.07	5.37	16.60	330

[a] Calculated for $C_{22}H_{18}Fe$: C, 78.12; H, 5.36; Fe, 16.51; mol. wt., 338. [b] Carbon analysis indicates that the compound is not completely pure.

TABLE III

REACTIONS OF DIFERROCENYLMERCURY AND *n*-BUTYLLITHIUM

(Diethyl ether-benzene soln., 25°, reactants then carbonated and hydrolyzed)

Molar ratio $(C_{10}H_9Fe)_2Hg$:*n*-C_4H_9Li	Time, min.	% yield, $FeC_{10}H_9CO_2H$
1:2	10	35
1:2	270	29
1:3	10	58
1:4	10	73, 80
1:8	10	73

various diarylmercury compounds react readily with *n*-butyllithium with formation of corresponding aryllithium derivatives and di-(*n*-butyl)-mercury. The direct metalation of ferrocene with *n*-butyllithium is complicated in that both mono- and 1,1′-dilithioferrocenes are produced, regardless of the ratio of reactants.[15] Metal interchange between diferrocenylmercury and *n*-butyllithium therefore might provide a convenient route to monolithioferrocene, uncontaminated by dilithioferrocene.[16]

It was found that diferrocenylmercury and *n*-butyllithium reacted readily in diethyl ether–benzene solution. Following carbonation and hydrolysis, both di-(*n*-butyl)-mercury and ferrocenemonocarboxylic acid were obtained. No trace of ferrocenedicarboxylic acid could be detected, indicating that mercury–lithium interchange occurs much more readily than does metalation.

Unfortunately, an appreciable molar excess of *n*-butyllithium was found to be required in order to bring about reasonably satisfactory conversion of diferrocenylmercury to monolithioferrocene (as evidenced by carbonation to the acid). Prolonged reaction periods did not appear to increase this conversion, nor did excesses of *n*-butyllithium greater than *ca.* 4:1. Possibly solvent systems other than the one used might promote the conversion when stoichiometric amounts of diferrocenylmercury and di-(*n*-butyl)-mercury are caused to react; this point is being investigated further. The results of the metal interchange experiments are summarized in Table III.

Experimental[17]

Materials.—Diferrocenylmercury[18] and di-(2-biphenylyl)-mercury[19] were prepared by published procedures. Di-(4-biphenylyl)-mercury, m.p. 217–217.5° (reported m.p. 216°[20]) was obtained by the reaction of 4-biphenylyllithium and mercuric chloride in diethyl ether to form 4-chloromercuribiphenyl (76% yield), followed by treatment of the chloromercuri derivative with sodium stannite[21] (second step, 33% yield).

Di-(3-biphenylyl)-mercury, a new compound, was prepared in a similar manner: 3-Bromobiphenyl (Aldrich Chemical Co.) was treated with an equimolar amount of *n*-butyllithium at room temperature for 1 hr. (carbonation of an aliquot followed by hydrolysis and acidification produced 3-biphenylcarboxylic acid, m.p., 157–159°; reported m.p., 160°[22]). Reaction of the resulting 3-biphenylyllithium with an equimolar amount of mercuric chloride in diethyl ether produced 3-chloromercuribiphenyl, m.p. 159–160° (70% crude yield). Crude 3-chloromercuribiphenyl (4.58 g.) was refluxed for 20 hr. with sodium iodide (7.50 g.) in 250 ml. of ethanol. The reaction mixture was filtered hot, and di-(3-biphenylyl)-mercury, m.p. 187–189°, crystallized from the filtrate (56% yield). A slightly purer product, m.p. 188.5–189°, was obtained by recrystallization of the material from *n*-heptane. *Anal.* Calcd. for $C_{24}H_{18}Hg$: C, 56.85; H, 3.58; Hg, 39.57. Found: C, 56.93; H, 3.83; Hg, 39.78.

Silver powder was obtained by reduction of silver chloride with dextrose.[23] G. E. lamp-grade nitrogen was used throughout this investigation.

Thermal Decomposition of Diferrocenylmercury in the Presence of Silver.—All reactions tabulated in Table I were carried out in a similar manner. A typical example

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

(16) Monolithioferrocene also has been prepared recently from chloromercuriferrocene and *n*-butyllithium [D. Seyferth and J. F. Helling, *Chem. & Ind.* (London), 1568 (1961)].

(17) All melting points are uncorrected. Analyses and molecular weight determinations were performed either by Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y., or by the analytical section of this (Monsanto) Laboratory.

(18) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954); M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

(19) G. Wittig and W. Herwig, *Chem. Ber.*, **88**, 962 (1955).

(20) A. Michaelis, *Ber.*, **28**, 595 (1895).

(21) For procedure, see: J. L. Maynard, *J. Am. Chem. Soc.*, **54**, 2119 (1932).

(22) L. Olgiati, *Ber.*, **27**, 3390 (1894).

(23) G. Brauer, "Handbuch der Praparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 766.

is given: An intimate mixture of diferrocenylmercury (0.0015 mole, 0.86 g.) and silver powder (0.012 g.-atom, 1.30 g.) was added under nitrogen to a Schlenk tube modified for sublimation. The tube was heated for 17 hr. in a bath of Wood's metal maintained at 265 ± 3°. Two distinct yellow-orange sublimates were deposited on the sides of the tube. The sublimates were collected, dissolved in *ca.* 30 ml. of hot *n*-heptane, filtered from a little silver powder, and cooled. There separated 0.24 g. of dark orange crystals of biferrocenyl; m.p., 237–239° dec. The infrared spectrum (Nujol) of biferrocenyl obtained in this manner was completely identical to the spectrum of biferrocenyl obtained previously.[4,5] The filtrate was chromatographed on alumina, producing 0.08 g. (29% yield) of ferrocene and an additional 0.01 g. of biferrocenyl. The total biferrocenyl yield was 0.30 g., or 54%.

In several experiments, the reaction residue following separation of the sublimation products was collected and finely powdered in a mortar. The powdered residue was extracted repeatedly with boiling xylene, then benzene, and finally dried at 110°. The residue then was carefully analyzed for its carbon, hydrogen, and iron content. Since the percentage of hydrogen was quite low, large (50–60 mg.) samples were used in combustion analyses to ensure high accuracy and reproducibility in the hydrogen determination. In a typical experiment, the analysis of the residue was: C, 5.72; H, 0.44; Fe, 2.30. Calculating the gram-atoms of each element and letting the value for carbon be 10.0, the ratio of gram-atoms of carbon:hydrogen:iron is 10.0:9.0:0.9. In another such analysis, the ratio was 10.6:7.6:1.1. These ratios approximate those required for the presence of polyferrocenylene $[(C_{10}H_8Fe)_x]$ in the residue.

In an experiment in which diferrocenylmercury was heated alone at 265° for 17 hr., workup of the products as described above produced ferrocene and biferrocenyl in yields of 68 and 13%, respectively.

In a control experiment in which diphenylmercury and silver were caused to react in the molar proportions described above for 2 hr. at 290–300°, biphenyl was formed in 77% yield.

Formation of Arylferrocenes from Diferrocenylmercury, Diarylmercury Compounds, and Silver.—All arylferrocenes described in Table II were prepared in the same manner. A typical example is given: An intimate mixture of diferrocenylmercury (0.00217 mole, 1.24 g.), diphenylmercury (0.00217 mole, 0.77 g.), and silver powder (0.032 g.-atom, 3.45 g.) was heated as described above for 22 hr. between 235 and 300°. The resulting sublimate was collected and chromatographed in hexane on alumina. There was produced 0.12 g. of a mixture of biphenyl and ferrocene, 0.51 g. of phenylferrocene, m.p. 109–112° (45% yield), and 0.19 g. of biferrocenyl. Recrystallization of the phenylferrocene from *n*-heptane produced orange leaflets; m.p., 111–112° (reported m.p., 114–115°[24]). A mixed melting point of the material with phenylferrocene obtained by the diazonium method[24] was not depressed, and the infrared spectra (KBr) of phenylferrocene obtained by both methods were identical.

4-Biphenylylferrocene also was obtained by the reaction of 4-biphenylyldiazonium chloride and ferrocene in glacial acetic acid (for the procedure, see ref. 24). Following chromatography of the products on alumina, 4-biphenylferrocene, m.p. 164–165°, was isolated in 41% yield. Higher arylated ferrocenes were noted but were not characterized further. A mixed melting point of samples of 4-biphenylylferrocene from both the diazonium and organomercury decomposition methods was undepressed, and the infrared spectra (KBr) of both samples were identical.

Reaction of Diferrocenylmercury and *n*-Butyllithium.—An example illustrating the reactions described in Table III is given: To a stirred suspension of diferrocenylmercury (0.0015 mole, 0.86 g.) in 40 ml. of a 1:1 mixture of diethyl ether and benzene (both solvents previously dried over sodium) under nitrogen was added 0.012 mole of *n*-butyllithium in 15 ml. of diethyl ether. The contents of the flask quickly became nearly homogeneous. After the mixture had been stirred for 10 min. it was carbonated, hydrolyzed, and acidified in the usual manner. The yellow precipitate of ferrocenemonocarboxylic acid, 0.50 g., dec. 207–209° (reported m.p., 210° dec.[25]), was washed with water and dried.

Anal. Calcd. for $C_{11}H_{10}FeO_2$: C, 57.44; H, 4.38; Fe, 24.28. Found: C 57.33; H, 4.52; Fe, 24.32.

A sample of 0.25 g. of this acid completely dissolved in 25 ml. of hot benzene; under these conditions ferrocene-1,1′-dicarboxylic acid is almost completely insoluble. A mixed melting point of the acid with an authentic sample of ferrocenemonocarboxylic acid was not depressed, and the infrared spectra (KBr) of both acids were identical. Chromatography of the ether–benzene soluble material produced a trace of ferrocene and several drops of di-(*n*-butyl)-mercury (infrared spectrum identical to that of an authentic sample).

In another reaction, the ferrocene-acid was esterified with methanol containing a drop of sulfuric acid. Chromatography of the products on alumina produced monocarbmethoxyferrocene, m.p. 69–70° (reported m.p. 70–71°[26]), as the only isolable product.

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[24] M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959).

[25] M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953.

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