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ORGANOMETALLIC COMPOUNDS

XVII*. BENZOYLATION OF BIFERROCENE AND SOME TRANSFORMATION REACTIONS OF THE BENZOYL DERIVATIVES

KOJI YAMAKAWA*, MASAO HISATOME, YOSHITAKA SAKO and SHIGETO ICHIDA
Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162 (Japan)

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Summary

The benzoylation of biferrocene (I) by the Friedel—Crafts reaction and some related reactions are described. 1'-Benzoylbiferrocene (II) and 1',1'''-dibenzoylbiferrocene (III) have been isolated. III has also been prepared by the Ullmann reaction of 1'-benzoyl-1'-bromoferrocene (VI). Some transformation reactions of the benzoylbiferrocenes (II and III) and the reactivity of the derivatives are briefly discussed.

Since the synthesis of biferrocene, a dimer of ferrocene, by Goldberg and Mayo [1] in 1959, only acetylation [2-5] and formylation [6] have been reported in studies of substitution reactions of biferrocene**. On the other hand, the reactivity of ferrocene and synthesis of its derivatives have been investigated in detail. The reasons for the few investigations of biferrocene are probably due to its lower reactivity [2,3] and the difficulty of isolating and purifying the many possible isomers produced. However, a comparison between the reactivity and structure of ferrocene and biferrocene or their derivatives is interesting and analogous with the relation between benzene and biphenyl. One of us (K.Y.) [2] has already reported on the acetylation of biferrocene and the isolation of the some product isomers. In this paper we describe the benzoylation of biferrocene, the preparation of 1',1'''-dibenzoylbiferrocene by an alternative route, and some transformation reactions of the benzoyl derivatives.

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* For Part XVI see ref. 17.

** Rausch briefly described in 1960 [7] the acetylation and benzoylation of biferrocene together with synthesis of biferrocene, but not the isolation and the detailed physical properties of the products.

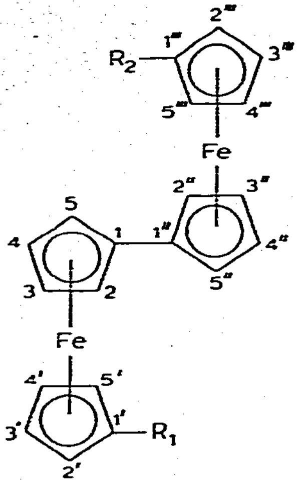


Fig. 1. Nomenclature system of biferrocenes (following Chemical Abstracts). It has been shown by X-ray crystallography [8] that the conformation of biferrocene is *trans* in solid state.

Results and discussion

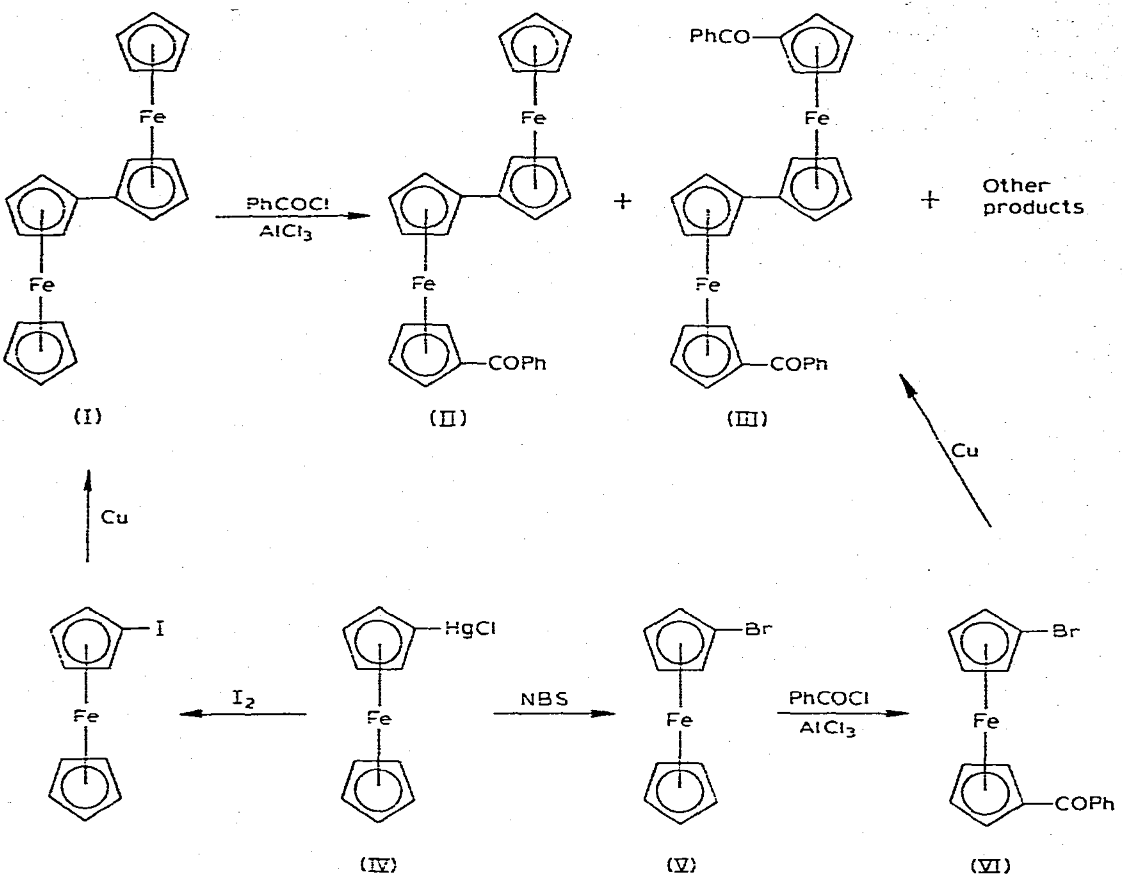
The Friedel—Crafts benzoylation of biferrocene with benzoyl chloride and $AlCl_3$ was carried out according to conventional methods. The crude product was column chromatographed on alumina, but separation of the several benzoylated biferrocenes into each component was very difficult due to overlap of their bands with each other, even if the solvent for elution was varied. Isolation of 1'-benzoyl- and 1',1'''-dibenzoyl-biferrocene was accomplished by repeated chromatography and recrystallization of the overlapping benzoylbiferrocene bands. Some other benzoylbiferrocenes in the mother liquor in recrystallization and in other unseparated chromatographic bands could not be isolated.

1'-Benzoylbiferrocene (II) (m.p. 135-136°C, M^+ 474, ν(C=O) 1622 cm^{-1}), obtained from the first portion of the overlapping bands eluted with benzene—ethyl acetate (10/1), had seventeen protons of Cp rings resonating in the range of δ 3.92-4.68 and five protons of a benzoyl group at δ 7.3-7.9 in its PMR spectrum. In the signals of the Cp ring protons there were a sharp singlet at δ 3.92 (5H) and a triplet at δ 4.68 (2H), assigned to unsubstituted Cp ring protons ($H_{1'''}$—$H_{5'''}$) and α-protons ($H_{2'}$·$H_{5'}$) of benzoyl-Cp ring, respectively.

1',1'''-Dibenzoylbiferrocene (III), m.p. 165-166.5°C, was obtained by the purification of the third portion of the bands eluted with benzene—ethyl acetate (10/1). The high-resolution mass spectrum of III exhibited a molecular ion peak (*m/e* 578.0672) corresponding to the composition $C_{34}H_{26}Fe_2O_2$. Its PMR spectrum showed four signals at δ 4.17, 4.22, 4.33 and 4.64 (each signal 4H) and complex lines at δ 7.2-7.8 (10 H), assigned to substituted Cp ring protons and benzoyl protons, respectively. There was no singlet signal near δ 6.0, characteristic of unsubstituted Cp ring protons.

In order to prove the structure chemically and to obtain higher total yields, the synthesis of 1',1'''-dibenzoylbiferrocene by an alternative route analogous to that of 1',1'''-diacetylbiferrocene [9] was carried out using chloro-

SCHEME 1. SYNTHESES OF BENZOYLBIFERROCENES



mercuriferrocene (IV) as a starting material. The Friedel—Crafts reaction of bromoferrocene (V), obtained by treatment of IV with *N*-bromosuccinimide [10], with PhCOCl and $AlCl_3$ gave 1-benzoyl-1′-bromoferrocene (VI) as a red oil. The benzoyl derivative (VI; ν(C=O) 1639 cm^{-1}, ν(C—Br) 494 cm^{-1}) had a PMR spectrum in which the signals of a benzoyl group (δ 7.4-8.0, 5H, m), bromo-Cp (δ 4.10, 2H, t; δ 4.38, 2H, t) and benzoyl-Cp (δ 4.57, 2H, t; δ 4.92, 2H, t) ring protons appeared in a 5/4/4 intensity ratio, respectively. The two peaks *m/e* 368 and 370 of the molecular ion in the mass spectrum indicated the presence of a bromine atom. The Ullmann coupling of 1-benzoyl-1′-bromoferrocene (VI) with copper bronze at 120-130°C gave 1′,1‴-dibenzoylbiferrocene (III; 53%) and benzoylferrocene (29%), which could be isolated almost pure by column chromatography. The coupling product was identical with the disubstituted compounds (III) in the benzoylation of biferrocene by a mixture melting point determination and by spectral comparisons. A total yield of 1′,1‴-dibenzoylbiferrocene (III) by the alternative path was 27% based on chloromercuriferrocene, while that in the benzoylation of biferrocene was only 2.6%. The formation of benzoylferrocene in the coupling of VI is assumed to

TABLE 1

PRODUCT YIELDS IN THE BENZOYLATION OF BIFERROCENE (%)

PhCOCl/biferrocene mole ratio	Recovered biferrocene	II	III
1.0	38	46	—
2.0	7.2	58	—
4.0	6.3	36	5.2

be due to the elimination of a bromine from the starting material, since the yield increased to 49% at a reaction temperature of 100-125°C.

On the other hand, benzoylation of the monobenzoylbiferrocene assigned to 1′-substituted isomer (II) also gave 1′,1‴-dibenzoylbiferrocene (III) in a 26% yield. These results confirmed the structures of both benzoyl derivatives II and III.

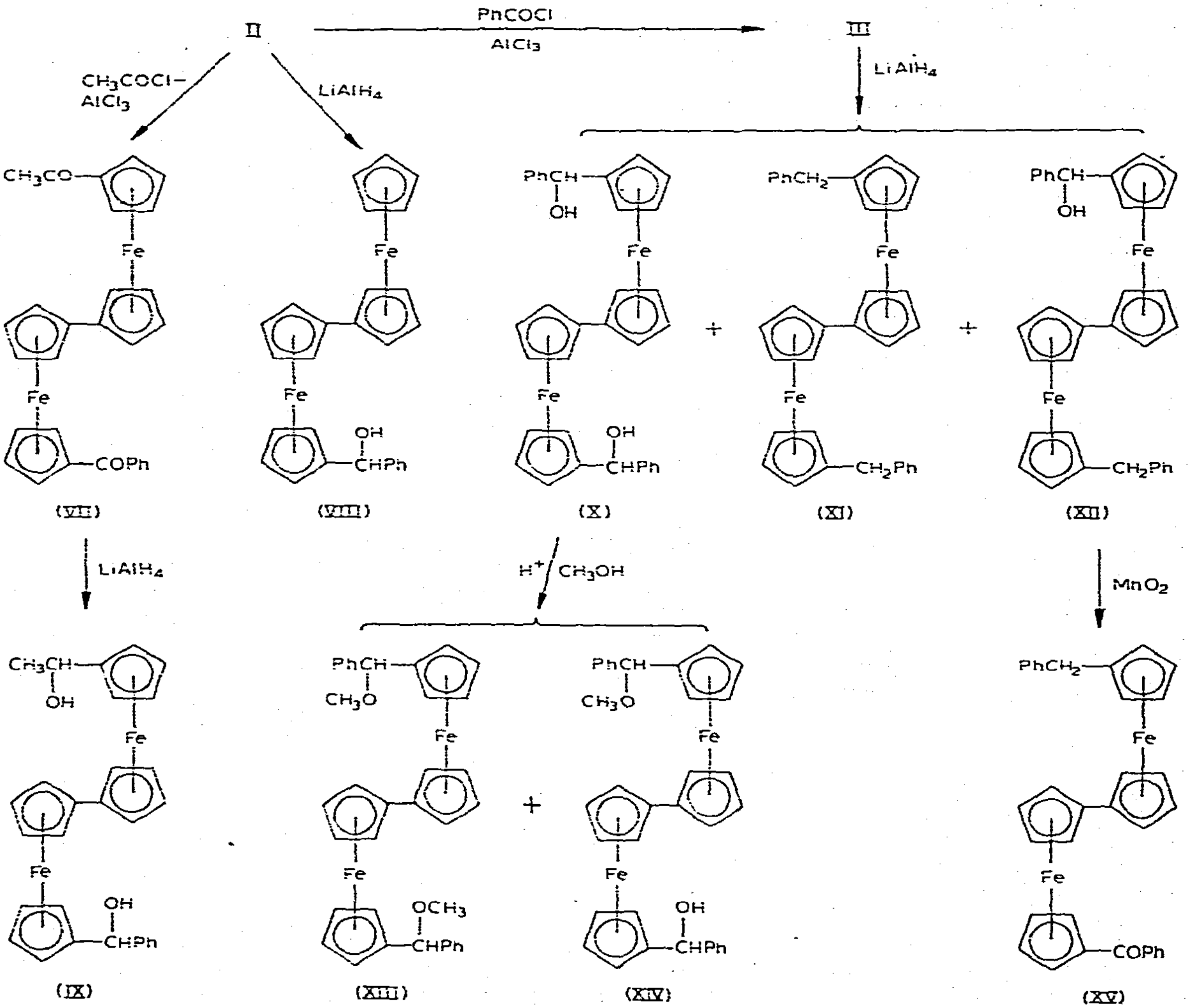
The yields of II and III depended on the mole ratio of PhCOCl to biferrocene, as shown in Table 1. Using a 2/1 ratio of PhCOCl/biferrocene, dibenzoylbiferrocene (III) was not obtained. The main-product in benzoylation of ferrocene was 1,1′-dibenzoylferrocene under similar conditions [11,12]. Even if a four fold molar amount of PhCOCl was used, the yield of III was only 5.2% although there remained some amounts of III which could not be isolated. Accordingly, it is confirmed that biferrocene is less reactive to benzoylation and acetylation [2,3] than is ferrocene.

1′-Benzoylbiferrocene (II) was acetylated by the Friedel—Crafts reaction with CH_3COCl and $AlCl_3$ to give 1′-acetyl-1‴-benzoylbiferrocene (VII), an asymmetrically substituted biferrocene. It exhibited a singlet of acetyl group at δ 2.10 (3H) and two triplets of acetylated Cp ring at δ 4.50 and δ 4.31 (both 2H) in the PMR, ν(C=O) of benzoyl and acetyl carbonyl groups at 1629 and 1657 cm^{-1} in the IR, and a molecular ion peak at *m/e* 516.0455 with a composition of $C_{29}H_{24}Fe_2O_2$ in the high-resolution mass spectrum.

Benzoyl derivatives II, III, and VII were subsequently reduced with $LiAlH_4$ to give the corresponding hydroxyl derivatives VIII, X, and IX, respectively, in which ν(C=O) absorption disappeared and ν(OH) appeared in the IR spectra. Reduction of dibenzoylbiferrocene (III) afforded 1′-benzyl-1‴-(α-hydroxybenzyl)biferrocene (XII; 19%) and 1′,1‴-dibenzylbiferrocene (XI; 5.8%), which would be formed by partial and entire hydrogenolysis, respectively, together with a normal reduction product (X; 74%). Use of larger excess $LiAlH_4$ increased the yield of dibenzylbiferrocene (XI; 63%) and decreased that of the two hydroxybiferrocenes (X: 18%, XII: 12%). In the reduction of 1′-benzoylbiferrocene (II), benzoylferrocene [13] and 1,1′-dibenzoylferrocene [12] under similar conditions, benzyl derivatives have not been produced.

In the mass spectrum of diol X at 70 eV, there appeared unusual fragment ions of *m/e* 566 ($[M-O]^+$) and *m/e* 550 ($[M-O_2]^+$) corresponding to the molecular ion peaks of XII and XI, respectively, in high intensity but no molecular ion of X (*m/e* 582) [14]. By lowering the ionization potential to 30 eV, the molecular ion peak of X appeared in a 4.9% intensity. On the other hand, the mass spectra of the compounds VIII, XII, IX at 70 eV, which have one hydroxy-

SCHEME 2. TRANSFORMATION REACTIONS OF BENZOYLBIFERROCENE DERIVATIVES



benzyl group, exhibited molecular ion peaks, together with the fragment ion peaks resulting from elimination of an oxygen.

Furthermore, it was confirmed by the PMR spectrum* that a stable α-biferrocenylcarbonium ion XVI, a dication, was formed at room temperature by dissolution of diol X into trifluoroacetic acid while the alcohol VIII decomposed immediately on dissolving in the acid even at −15°C. The PMR data of dication XVI are very similar to those for the ion XVII reported already by us [15] (Table 2).

These spectral results would reflect the unusual behaviour revealed by the reduction of III. It is likely that the formation of the benzyl group arises from

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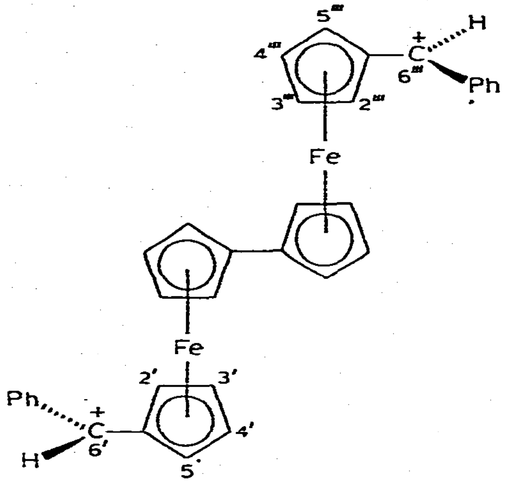
* The results in the PMR spectra of biferrocenylcarbonium ions will be discussed in detail in a forthcoming paper.

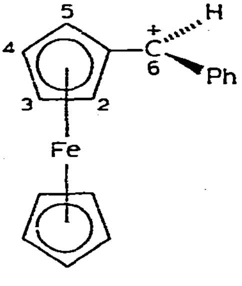
TABLE 2

THE PMR DATA OF α-FERROCENYLCARBONIUM IONS XVI AND XVII IN TRIFLUOROACETIC ACID (IN δ, ppm)

	$H_{5'}$, $H_{5'''}$	$H_{2'}$, $H_{2'''}$	$H_{4'}$, $H_{4'''}$	$H_{3'}$, $H_{3'''}$	$H_{6'}$, $H_{6'''}$
XVI	4.88	5.31	6.10	6.35	8.12
	H_5	H_2	H_4	H_3	H_6
XVII [15]	4.77	5.52	6.24	6.45	8.09



(XVI)



(XVII)

the stability of the α-ferrocenylcarbonium ion, and that the hydroxyl derivative of biferrocene with symmetrical structure is able to become a more stable carbonium ion than the unsymmetrical biferrocene derivative.

In addition, methanol—aq. HCl solution of diol X was refluxed to give 1',1'''-bis(α-methoxybenzyl)biferrocene (XIII) and 1'-(α-hydroxybenzyl)-1'''-(α-methoxybenzyl)biferrocene (XIV). Benzylbiferrocene (XII) was converted to 1'-benzoyl-1'''-benzylbiferrocene (XV) by oxidation with MnO_2. The structures of these products were confirmed by spectroscopy.

Experimental

All melting points are uncorrected. Column-chromatographic separations were carried out with Wako activated alumina (300 mesh). IR spectra were measured using a Hitachi—Perkin—Elmer model 225 grating infrared spectrophotometer using KBr disks or liquid films. PMR spectra were measured on a JEOL JNM-4H-100 spectrometer at 100 MHz at room temperature with TMS as an internal reference. The spectra of biferrocenylcarbonium ion XVI were recorded at room temperature immediately after dissolution of the diol X in commercial 100% trifluoroacetic acid at a temperature below —10°C. Mass spectra were obtained with a Hitachi RMU-7M double focussing mass spectrometer or a JEOL JMS-01SG double focussing mass spectrometer with a direct insertion probe, at 30 or 70 eV ionizing energy. Numbers in parentheses indicate relative intensities of the peaks versus intensity of the base peak.

Chloromercuriferrocene [10] (m.p. 197-199°C), bromoferrocene [10] (m.p. 31-32°C) and biferrocene [5,8] (m.p. 236-237°C) used in this work were prepared by procedures previously reported.

Benzoylation of biferrocene (I)

Distilled PhCOCl (1.52 g, 10.8 mmol) in 30 ml of dry CH_2Cl_2 were added with vigorous mechanical stirring to a suspension of anhydrous $AlCl_3$ (1.60 g, 12.0 mmol) in a CH_2Cl_2 solution (50 ml) of biferrocene (I; 1.00 g, 2.70 mmol) free from trace ferrocene. The reaction mixture was refluxed with stirring for 1.5 h, and then was poured into ice-water. The resulting hydrolysate was phase separated after the reduction of ferricinium ion with added ascorbic acid. The organic layer was washed with saturated aq. $NaHCO_3$ and then water, dried with $CaCl_2$ and evaporated. The red oily residue was chromatographed on alumina. Small amounts of ferrocene (14 mg), possibly resulting from cleavage of biferrocene with $AlCl_3$, and 60 mg of recovered I (6%) were eluted with hexane and benzene, respectively. The first portion of the following red band eluted with 10/1 benzene—ethyl acetate was rechromatographed several times to remove the overlapping subsequent bands. Recrystallization of this material from hexane—benzene three times gave 454 mg (36%) of 1′-benzoylbiferrocene (II) as red-orange needles, m.p. 135-136°C. (Found: C, 68.52; H, 4.59. $C_{27}H_{22}Fe_2O$ calcd.: C, 68.39; H, 4.68%). IR spectrum (KBr, cm^{-1}): 1622 [ν(C=O)], 1595 [ν(C=C) of Ph]. PMR spectrum ($CDCl_3$, δ): 3.92 (5H, s, unsubst. Cp ring), 4.13 (2H; t, $H_{3''}$,$H_{4''}$), 4.20 (2H; t, H_3,H_4), 4.24 (2H; m, H_2,H_5), 4.34 (4H; m, $H_{3'}$,$H_{4'}$,$H_{2''}$,$H_{5''}$), 4.68 (2H; t, $H_{2'}$,$H_{5'}$), 7.3-7.9 (5H; m, Ph ring). Mass spectrum (70 eV, *m/e*): 474 (100, M^+), 409 (67, $[M—C_5H_5]^+$), 381 (40, $[M—(C_5H_5 + CO)]^+$, 304 (23, $[M—(C_5H_5 + COPh)]^+$).

The second portion eluted with 10/1 benzene—ethyl acetate was a mixture of unknown products (151 mg) which could not be separated into each component. The third portion collected by elution with the same solvent was rechromatographed several times until the portion was approximately one band. The red solid obtained was recrystallized from hexane—benzene to yield 86 mg (5.2%) of 1′,1‴-dibenzoylbiferrocene (III) as deep-red-brown needles, m.p. 165-166.5°C. (Found: C, 70.78; H, 4.47; M^+ 578.0672. $C_{34}H_{26}Fe_2O_2$ calcd.: C, 70.62; H, 4.53%; mol. wt. 578.0631.) IR spectrum (KBr, cm^{-1}): 1623 [ν(C=O)], 1593 [ν(C=C) of Ph]. PMR spectrum ($CDCl_3$, δ): 4.17 (4H; m, H_3, H_4, $H_{3''}$, $H_{4''}$), 4.22 (4H; m, H_2, H_5, $H_{2''}$, $H_{5''}$), 4.33 (4H; t, $H_{3'}$, $H_{4'}$, $H_{3'''}$, $H_{4'''}$), 4.64 (4H; t, $H_{2'}$, $H_{5'}$, $H_{2'''}$, $H_{5'''}$), 7.2-7.8 (10H; m, Ph ring). Mass spectrum (70 eV, *m/e*): 578 (58, M^+), 409 (100, $[M—C_5H_4COPh]^+$), 381 (56, $[M—(C_5H_4\text{-}COPh + CO]^+$), 304 (20, $[M—(C_5H_4COPh + COPh]^+$).

Using equal and double molar amounts of PhCOCl to biferrocene (I) 1′-benzoylbiferrocene (II) was produced in 46 and 58% yield, respectively, after purification, but the dibenzoylbiferrocene (III) was not isolated.

1-Benzoyl-1′-bromoferrocene (VI)

$AlCl_3$ (1.95 g, 14.6 mmol) was suspended in a CH_2Cl_2 solution (150 ml) of PhCOCl (1.76 g, 12.6 mmol). Bromoferrocene (V; 1.00 g, 3.78 mmol) in

CH_2Cl_2 (50 ml) was added to the above suspension with vigorous stirring at 0°C. The reaction mixture was stirred for 3 h at the same temperature and then poured into ice-water. After adding ascorbic acid, the hydrolysate was phase separated. The organic layer was washed with saturated aq. Na_2CO_3 and water dried with Na_2SO_4 and evaporated. The red oily residue was chromatographed on alumina to separate into two bands. The first band eluted with hexane was a mixture of ferrocene and the recovered bromoferrocene (V; 309 mg), identified by GLC. The second band eluted with benzene—ethyl acetate (10/1) was 1-benzoyl-1'-bromoferrocene (VI; 771 mg, 55%), a red oil, which was purified by rechromatography. Mass spectrum (70 eV, *m/e*): 370 (49, M^+, containing ^{81}Br), 368 (52, M^+, containing ^{79}Br), 105 (100, $PhCO^+$). IR spectrum (liq. film, cm^{-1}): 1639 [ν(C=O)], 1597 [ν(C=C) of Ph], 494 [ν(C—Br)]. PMR spectrum ($CDCl_3$, δ): 4.10 and 4.38 (4H, each t, Cp-Br), 4.57 and 4.92 (4H, each t, benzoyl-Cp), 7.35-8.0 (5H, m, Ph).

1-Benzoyl-1'-bromoferrocene oxime, which was derived from VI according to the standard method [16], was orange-yellow prisms, m.p. 146-147°C. Observed M^+ 384.9595; $C_{17}H_{14}{}^{81}BrFeNO$ calcd.: 384.9588 and observed M^+ 382.9609, $C_{17}H_{14}{}^{79}BrFeNO$ calcd.: 382.9608. IR spectrum, (KBr, cm^{-1}): 3200 [ν(O—H)], 1629 [ν(C=N)], 1598 [ν(C=C) of Ph], 488 [ν(C—Br)]. PMR spectrum ($CDCl_3$, δ): 4.1-4.8 (8H, m, Cp), 7.35-7.6 (5H, m, Ph). Mass spectrum (70 eV, *m/e*): 385 (46, M^+), 383 (49, M^+), 369 (97, $[M-O]^+$), 367 (100, $[M-O]^+$).

The Ullmann reaction of 1-benzoyl-1'-bromoferrocene (VI)

A mixture of 1-benzoyl-1'-bromoferrocene (VI; 2.7 g, 7.2 mmol) and 26 g of activated copper was heated at 120-130°C for 37 h in a flask fitted with a glass tube. After cooling to room temperature the reaction mixture was repeatedly extracted with CH_2Cl_2 until the dichloromethane extracts appeared colorless. The extracts were evaporated and chromatographed on alumina. The first band eluted with benzene—ethyl acetate (20/1) yielded benzoylferrocene (0.61 g; 29%). Continued elution with 5/1 benzene—ethyl acetate afforded 1',1'''-dibenzoylbiferrocene (III; 1.10 g, 53%). This compound was recrystallized to give red-brown needles, m.p. 166-167°C, which was identified with III obtained by benzoylation of biferrocene.

The yields of the coupled products depended on reaction temperature; at 75-85°C (26 h) III and the recovered VI were obtained in 3 and 78% yields, respectively, and at 100-125°C (36 h) III and benzoylferrocene in 12 and 49% yields.

Benzoylation of 1'-benzoylbiferrocene (II)

The Friedel—Crafts reaction of 1'-benzoylbiferrocene (100 mg, 0.21 mmol) with PhCOCl (30 mg, 0.21 mmol) and $AlCl_3$ (40 mg, 0.30 mmol) in CH_2Cl_2 (15 ml) was carried out according to the same procedure as benzoylation of biferrocene. The unresolved two bands eluted with 10/1 benzene—ethyl acetate were separated into two portions. Each portion was purified by chromatography and recrystallization. From the first and second portions, respectively, 26 mg of the recovered II (26%) and 32 mg of 1',1'''-dibenzoylbiferrocene (III; 26%) were obtained. The latter was shown to be identical with III obtained by benzoylation of biferrocene by a comparison of their spectra.

Acetylation of 1'-benzoylbiferrocene (II)

Using 100 mg of 1'-benzoylbiferrocene (II; 0.21 mmol), 16 mg of distilled CH_3COCl (0.21 mmol), 40 mg of $AlCl_3$ (0.30 mmol) and 15 ml of CH_2Cl_2, the acetylation was carried out according to a procedure similar to the above benzoylation. By chromatography on alumina, the crude reaction mixture was separated into the starting material (46 mg) and an acetylated product (44 mg, 41%). These were eluted with 10/1 and 4/1 benzene—ethyl acetate, respectively. On recrystallization of the latter from benzene—hexane, 1'-acetyl-1'''-benzoylbiferrocene (VII) was obtained as deep-red-brown needles, m.p. 129.5-130.5°C. (Found: C, 67.94; H, 4.57; M^+ 516.0455. $C_{29}H_{24}Fe_2O_2$ calcd.: C, 67.48; H, 4.96%; mol. wt. 516.0474.) IR spectrum (KBr, cm^{-1}): 1657 [ν(C=O) of acetyl], 1629 [ν(C=O) of benzoyl], 1595 [ν(C=C) of Ph], 1371 [$\delta(CH_3)$]. PMR spectrum ($CDCl_3$, δ): 2.10 (3H, s, methyl of acetyl), 4.15 (2H, m, H_3, H_4), 4.24 (6H, m, H_2, H_5, $H_{2''}$—$H_{5''}$), 4.31 (2H, t, $H_{3'}$, $H_{4'}$), 4.33 (2H, t, $H_{3'''}$, $H_{4'''}$), 4.50 (2H, t, $H_{2'}$, $H_{5'}$), 4.65 (2H, t, $H_{2'''}$, $H_{5'''}$), 7.3-7.8 (5H, m, Ph). Mass spectrum (70 eV, *m/e*): 516 (92, M^+), 409 (100, $[M—C_5H_4COCH_3]^+$), 381 (47, $[M—(C_5H_4COCH_3 + CO)]^+$), 347 (28, $[M—C_5H_4COPh]^+$), 319 (15, $[M—(C_5H_4COPh + CO)]^+$), 304 (31, $[M—(C_5H_4COCH_3 + COPh)]^+$).

1'-(α-hydroxybenzyl)biferrocene (VIII)

To a suspension of $LiAlH_4$ (296 mg) in 10 ml of absolute ether, 50 ml of ether—benzene solution (3/1) of 1'-benzoylbiferrocene (II; 283 mg) was added with stirring at room temperature. The mixture was refluxed for 0.5 h on a steam bath. When cooled, AcOEt was added to decompose the excess reagent. A mixture of ether—ethanol—water (8/4/0.5) was then added to the above reactant and the resulting yellow suspension was filtered, dried over Na_2SO_4 and evaporated. The residue (276 mg, 98%) was recrystallized from hexane to give 1'-hydroxybenzoylbiferrocene (VIII), m.p. 121-122°C, as yellow needles. (Found: C, 68.32; H, 5.21; M^+ 476.0492. $C_{27}H_{24}Fe_2O$ calcd.: C, 68.10; H, 5.08%; mol. wt. 476.0523.) IR spectrum (KBr, cm^{-1}): 3540 [ν(O—H)], 1598 [ν(C=C) of Ph]. PMR spectrum ($CDCl_3$, δ): 3.97, 4.22, and 4.40 [17H, each m, Cp ring), 2.17 (1H, d, OH), 5.26 (1H, d, methine with Ph), 7.15-7.45 (5H, m, Ph). Mass spectrum (70 eV, *m/e*): 476 (80, M^+), 474 (40, $[M—H_2]^+$), 460 (100, $[M—O]^+$), 409 (15, $[M—(H_2 + C_5H_5)]^+$), 304 (96, $[M—(C_5H_5 + CH(OH)Ph)]^+$).

1'-(α-Hydroxybenzyl)-1'''-(α-hydroxyethyl)biferrocene (IX)

Reduction of 1'-acetyl-1'''-benzoylbiferrocene (VII; 100 mg) with $LiAlH_4$ (100 mg) in ether—benzene was carried out in a manner similar to the reduction of II. The residue evaporated was chromatographed with ethyl acetate as a eluent to give 15 mg of unknown product, possibly a mixture of the partial reduction products, and 67 mg of 1'-(α-hydroxybenzyl)-1'''-(α-hydroxyethyl)biferrocene (IX; 67%). Recrystallization of crude IX gave yellow needles, m.p. 115-117°C. (Found: C, 66.78; H, 5.41; M^+ 520.0814. $C_{29}H_{28}Fe_2O_2$ calcd.: C, 66.95; H, 5.43%; mol. wt. 520.0788.) IR spectrum (KBr, cm^{-1}): 3515 and 3417 [ν(O—H)], 1595 [ν(C=C) of Ph], 1370 [$\delta(CH_3)$]. PMR spectrum (acetone-d_6, δ): 1.29 (3H, d, CH_3), 3.90, 4.21, and 4.48 (16H, each m, Cp ring), 4.45 (1H, m, methine with CH_3, assigned by decoupling method), 5.40 (1H, d, methine with Ph), 7.15-7.45 (5H, m, Ph). Mass spectrum (70 eV, *m/e*): 520 (11, M^+), 502 (57,

$[M-H_2O]^+$), 486 (49, $[M-(H_2O + O)^+]$), 304 (100, $[M-(C_5H_4CH(OH)CH_3 + CH(OH)Ph)]^+$).

Reduction of 1′,1‴-dibenzoylbiferrocene (III)

Reduction of 1′,1‴-dibenzoylbiferrocene (III; 474 mg) with $LiAlH_4$ (228 mg) in ether—benzene (170 ml) was carried out according to the procedure for the reduction of II. The resulting residue evaporated was chromatographed on alumina to separate into three bands. The first band compound (26 mg, 5.8%) eluted with benzene was recrystallized from hexane—benzene to give 1′,1‴-dibenzylbiferrocene (XI), yellow needles, m.p. 151.5-153°C. (Found: C, 74.09; H, 5.73. $C_{34}H_{30}Fe_2$ calcd.: C, 74.21; H, 5.50%.) IR spectrum (KBr, cm^{-1}): 2925, 2902 [ν(C—H)], 1597 [ν(C=C) of Ph]. PMR spectrum ($CDCl_3$, δ): 3.38 (4H, s, benzyl protons), 3.87, 4.12, and 4.25 (16H, m, Cp ring), 7.0-7.3 (10H, m, Ph). Mass spectrum (70 eV, *m/e*): 550 (100, M^+), 395 (16, $[M-C_5H_4CH_2Ph]^+$), 304 (24, $[M-(C_5H_4CH_2Ph + CH_2Ph)]^+$).

The second band eluted with benzene—ethyl acetate (1/5) yielded 1′-benzyl-1‴-(α-hydroxybenzyl)biferrocene (XII; 87 mg, 19%), which was recrystallized from hexane—benzene to give yellow needles, m.p. 144-146°C. (Found: C, 72.00; H, 5.49; M^+ 566.1004. $C_{34}H_{30}Fe_2O$ calcd.: C, 72.11; H, 5.34%; mol. wt. 566.9995.) IR spectrum (KBr, cm^{-1}): 3545 [ν(O—H)], 2925, 2908 [ν(C—H)]. PMR spectrum ($CDCl_3$, δ): 2.15 (1H, d, OH), 3.35 (2H, s, benzyl protons), 3.85, 3.95, 4.05, 4.15, 4.18, 4.29, and 4.34 (16H, each m, Cp ring), 5.20 (1H, d, methine with Ph), 6.95-7.30 (10H, m, Ph). Mass spectrum (70 eV, *m/e*): 566 (15, M^+), 564 (23, $[M-H_2]^+$), 550 (100, $[M-O]^+$), 304 (31, $[M-(C_5H_4CH(OH)Ph + CH_2Ph)]^+$).

The third band eluted with ethyl acetate yielded 1′,1‴-bis(α-hydroxybenzyl)biferrocene (X; 357 mg, 74%), which was recrystallized from hexane—benzene to give yellow needles, m.p. 164-165.5°C. (Found: C, 70.70; H, 5.17; M^+ 582.0966 at 30 eV. $C_{34}H_{30}Fe_2O_2$ calcd.: C, 70.13; H, 5.19%; mol. wt. 582.0944.) IR spectrum (KBr, cm^{-1}): 3540 [ν(O—H)], 1596 [ν(C=C) of Ph]. PMR spectrum (DMSO-d_6, δ): 3.67, 3.83, 4.05, 5.14, and 4.39 (16H, each m, Cp ring), 5.16 (2H, d, OH), 5.33 (2H, d, methine with Ph), 7.2-7.4 (10H, m, Ph). Mass spectrum (70 eV, *m/e*): 580 (4.1, $[M-H_2]^+$), 578 (39, $[M-2H_2]^+$), 566 (6.8, $[M-O]^+$), 564 (68, $[M-H_2O]^+$), 550 (45, $[M-O_2]^+$), 409 (100, $[M-(H_2 + C_5H_4CH(OH)Ph)]^+$), 381 (61, $[M-(H_2 + O_2 + C_5H_4CH(OH)Ph)]^+$), 304 (35); at 30 eV, *m/e*: 582 (4.9, M^+), 580 (5.1), 578 (9.1), 566 (18), 564 (51), 550 (100), 409 (51), 381 (38), 304 (45).

Using 957 mg of the starting material and 1.21 g of $LiAlH_4$, the yields of XI, XII, and X were 575 mg (63%), 109 mg (12%) and 173 mg (18%), respectively.

1′,1‴-Bis(α-methoxybenzyl)biferrocene (XIII) and 1′-(α-hydroxybenzyl)-1‴-(α-methoxybenzyl)biferrocene (XIV)

1′,1‴-Bis(α-hydroxybenzyl)biferrocene (X; 104 mg) in methanol (150 ml) containing 10% aq. HCl (0.5 ml) was refluxed for 1 h. After the methanol of the reaction mixture was distilled off, the residue was extracted with ether, washed with Na_2CO_3 and water and evaporated. Upon chromatography, the first band eluted with benzene yielded 1′,1‴-bis(α-methoxybenzyl)biferrocene (XIII; 48 mg, 44%), which was recrystallized from hexane—benzene to give yellow needles, m.p. 154-155.5°C. Mass spectrum (70 eV), M^+ 610.1258 ($C_{36}H_{34}Fe_2O_2$ calcd.: 610.1257); m/e 610 (100, M^+), 580 (23, $[M{-}CH_2O]^+$), 550 (14, $[M{-}2CH_2O]^+$). IR spectrum (KBr, cm^{-1}): 1090 [ν(C—O—C)]. PMR spectrum ($CDCl_3$, δ): 3.19 (6H, s, OCH_3), 3.69, 3.87, 4.03, and 4.18 (16H, each m, Cp ring), 4.78 (2H, s, methine with OCH_3), 7.30 (10H, s, Ph).

The second band eluted with 1/1 benzene—ethyl acetate yielded 1′-(α-hydroxybenzyl)-1‴-(α-methoxybenzyl)biferrocene (XIV; 40 mg, 38%), which was recrystallized from hexane—benzene to give yellow needles, m.p. 130-134.5°C IR spectrum (KBr, cm^{-1}): 3500 [ν(O—H)]. PMR spectrum ($CDCl_3$, δ): 2.15 (1H, d, OH), 3.19 (3H, s, OCH_3), 3.81-4.40 (16H, m, Cp ring), 4.79 (1H, s, methine with OCH_3), 5.23 (1H, s, methine with OH), 7.23 and 7.32 (each 5H, s, Ph).

The third band compound eluted with ethyl acetate was recovered diol X (8 mg).

1′-Benzoyl-1‴-benzylbiferrocene (XV)

A benzene solution (100 ml) of 1′-benzyl-1‴-(α-hydroxybenzyl)biferrocene (XII; 116 mg) was refluxed with MnO_2 for 1 h. After the mixture was filtered, the filtrate was evaporated and chromatographed. Elution with 50/1 benzene—ethyl acetate yielded 1′-benzoyl-1‴-benzylbiferrocene (XV; 31 mg, 27%), which was recrystallized from hexane to give orange-red needles, m.p. 99.5-100°C. (Found: C, 72.72; H, 5.20. $C_{34}H_{28}Fe_2O$ calcd.: C, 72.37; H, 5.00%.) IR spectrum (KBr, cm^{-1}): 1623 [ν(C=O) of benzoyl]. PMR spectrum ($CDCl_3$, δ): 3.40 (2H, s, methylene of benzyl), 3.87, 4.14, and 4.23 (12H, each m, Cp ring except for benzoylated Cp ring), 4.37 and 4.72 (4H, each t, benzoylated Cp ring), 7.0-7.9 (10H, m, Ph). Mass spectrum (70 eV, m/e): 564 (100, M^+), 409 (79, $[M{-}C_5H_4CH_2Ph]^+$), 381 (55, $[M{-}(C_5H_4CH_2Ph + CO)]^+$).

Continued elutions with 5/1 and 1/1 benzene—ethyl acetate yielded 1′,1‴-dibenzoylbiferrocene (trace), identified by comparison with an authentic sample, and the recovered XII (57 mg, 49%).

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References

1 S.I. Goldberg and D.W. Mayo, Chem. & Ind., (1959) 671.
2 K. Yamakawa, N. Ishibashi, and K. Arakawa, Chem. Pharm. Bull. (Tokyo), 12 (1964) 119.
3 S.I. Goldberg and J.S. Crowell, J. Org. Chem., 29 (1964) 996.
4 A.N. Nesmeyanov, V.N. Drozd, V.A. Sazonova, V.I. Romanenko, A.K. Profov'ev and L.A. Nikonova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1963) 667.
5 M.D. Rausch, J. Org. Chem., 29 (1964) 1257.
6 M.D. Rausch and T.M. Gund, J. Organometal. Chem., 24 (1970) 463.
7 M.D. Rausch, J. Amer. Chem. Soc., 82 (1960) 2080.
8 (a) Z.L. Kaluskii, R.L. Avoyan, and Yu.T. Struchkov, Zh. Strukt. Khim., 3 (1962) 599.

(b) A.C. MacDonald and J. Trotter, Acta Crystallogr., 17 (1964) 872.
9 S.I. Goldberg and R.L. Matterson, J. Org. Chem., 29 (1964) 323.
10 R.W. Fish and M. Rosenblum, J. Org. Chem., 30 (1965) 1253.
11 R. Riemschneider and D. Helm, Chem. Ber., 89 (1956) 155.
12 M.D. Rausch, M. Vogel and H. Rosenberg, J. Org. Chem., 22 (1957) 903.
13 N. Weliky and E.S. Gould, J. Amer. Chem. Soc., 79 (1957) 2742.
14 M. Hisatome, S. Ichida and K. Yamakawa, Org. Mass Spectr. submitted for publication.
15 M. Hisatome and K. Yamakawa, Tetrahedron, 27 (1971) 2101.
16 K. Yamakawa and M. Hisatome, Tetrahedron, 26 (1970) 4483.
17 K. Yamakawa and M. Moroe, Chem. Pharm. Bull. (Tokyo), 22 (1974) 709.