Intramolecular Michael addition as a method for preparation of [*m*][5]ferrocenophanes
I. Synthesis of [5](1,1′)[5](3,4′)ferrocenophane-1,5-dione*

*P. ELEČKO and *E. SOLČÁNIOVÁ

*Department of Organic Chemistry, Faculty of Natural Sciences,
Komenský University, 816 31 Bratislava*

*Institute of Chemistry, Komenský University,
816 31 Bratislava*

Acetylation of [5]ferrocenophane afforded the isomeric diacetyl[5]ferrocenophanes. The basically catalyzed reaction of 4-chlorobenzaldehyde or benzaldehyde with 3,4′-diacetyl[5]ferrocenophane afforded, in addition to condensation products, also derivatives of [5](1,1′)[5](3,4′)ferrocenophane-1,5-dione. The basically catalyzed cyclization of 3-acetyl-4′-(4-chlorocinnamoyl)[5]ferrocenophane furnished a doubly bridged derivative of ferrocene.

Ацетилированием[5]ферроценофана были получены изомерные диацетил[5]ферроценофаны. Реакция 4-хлорбензальдегида или бензальдегида с 3,4′-диацетил[5]ферроценофаном, катализируемая основанием, приводит к образованию, кроме продуктов конденсации, производных [5](1,1′)[5](3,4′)-ферроценофан-1,5-диона. Замыканием круга 3-ацетил-4′-(4-хлорцинамоил)[5]ферроценофана, катализированного основанием, также образовалось двухмостиковое производное ферроцена.

Derivatives of [5]ferrocenophane-1,5-dione were prepared by an intramolecular Michael addition [2—7]. This method has been, however, attempted only once for preparation of doubly bridged derivatives [8].

This paper is aimed to check the possibilities to synthesize derivatives of [5][5]ferrocenophanes by an intramolecular Michael addition from suitable [5]ferrocenophane derivatives.

[5]Ferrocenophane, prepared from ferrocene [4] is a suitable starting material for construction of [5][5]ferrocenophanes. The acetylation of ferrocene can gi-

---

* Nomenclature and numbering of ferrocenophanes according to [1].

ve rise to only two monoacetyl derivatives, but to six diacetyl heteroannular derivatives, namely 3,4'-, 2,3'-, 2,4'-, 2,5'-, 2,2'-, and 3,3'-diacetyl[5]ferrocenophanes. Respecting the Dreiding models, five of them, excepting the 2,5'-derivative, can afford [5][5]ferrocenophane.

The construction of the second bridge can start either from diacetyl[5]ferrocenophanes (route *A*), or from X-acetyl-Y-cinnamoyl[5]ferrocenophanes (route *B*). Both possibilities were checked (Scheme 1).

Acetylation of [5]ferrocenophane with an excess of acetyl chloride and aluminium chloride afforded a mixture consisting of three diacetyl derivatives. The isomer of m.p. 126—127°C was assigned the structure *Ic* (3,4'-diacetyl derivative) according to analysis of ^{1}H-n.m.r. spectra and by comparing with the data of *Nesmeyanov et al.* [8]: Two multiplets at $\delta = 4.54$, corresponding to 2H and at $\delta = 4.44$ (4H) were found in the region of ferrocene proton shifts; the singlet of acetyl groups at $\delta = 2.38$ was overlapped by a multiplet of two methylene groups of the bridge. The multiplet of other three methylene groups of the bridge was at $\delta = 1.90$ (6H).

The product of m.p. 93—97°C was identified on the basis of ^{1}H-n.m.r. spectrum as 2,3'- or 2,4'-diacetyl derivative: 3 multiplets of a β-substituted ring appeared at $\delta = 4.65$ (1H), 4.57 (1H), and 4.44 (1H) and a multiplet at $\delta = 4.25$ (3H) corresponding to an α-substituted ring. Two singlets of acetyl groups α-COCH$_3$ and β-COCH$_3$ appeared at $\delta = 2.31$ (3H) and 2.40 (3H), respectively.

3,4'-Diacetyl[5]ferrocenophane (*Ic*) reacted with 4-chlorobenzaldehyde in ethanol at room temperature to give exclusively condensation products (*IIb* and *IIIa*); at reflux 3-(4-chlorophenyl)[5](1,1')[5](3,4')ferrocenophane-1,5-dione (*IVa*) was obtained. The structure of this [5][5]ferrocenophane was proved by elemental analysis and ^{1}H-n.m.r. spectrum, which showed a multiplet of aromatic protons at $\delta = 7.3$ (4H) and three multiplets in the region of ferrocene proton shifts at $\delta = 4.75$ (2H), 4.65 (2H), and 4.44 (3H). The multiplet at $\delta = 4.44$ contained, in addition to ferrocene protons also a multiplet of a methine proton ($>$CH—Ar). Protons of COCH$_2$ groups formed two doublet-doublets corresponding to two H$_A$ protons of COC$\begin{smallmatrix}H_A\\H_B\end{smallmatrix}$ groups at $\delta = 2.83$ ($J_{AB} \doteq J_{AC} = 12$ Hz). The second doublet-doublet was overlapped by a multiplet of two methylene groups of a pentamethylene bridge at $\delta = 2.4$ (6H) and the multiplet of three methylene groups of the above-mentioned bridge was located at $\delta = 1.95$ (6H). No maximum was found in the 305—320 nm region of the u.v. spectrum, which is characteristic of the chalcone systems and was present in both condensation products *IIb* and *IIIa*. The electron impact mass spectrum revealed the most intense peak of molecular ion at *m/z* 460; the next more intense peak appeared at *m/z* 281 after some less intense ones at *m/z* 432, 426, 401, and 340. The product *IVa* was isolated also when heating dicinnamoyl derivative *IIIa* in ethanolic sodium hydroxide. The ^{1}H-n.m.r.
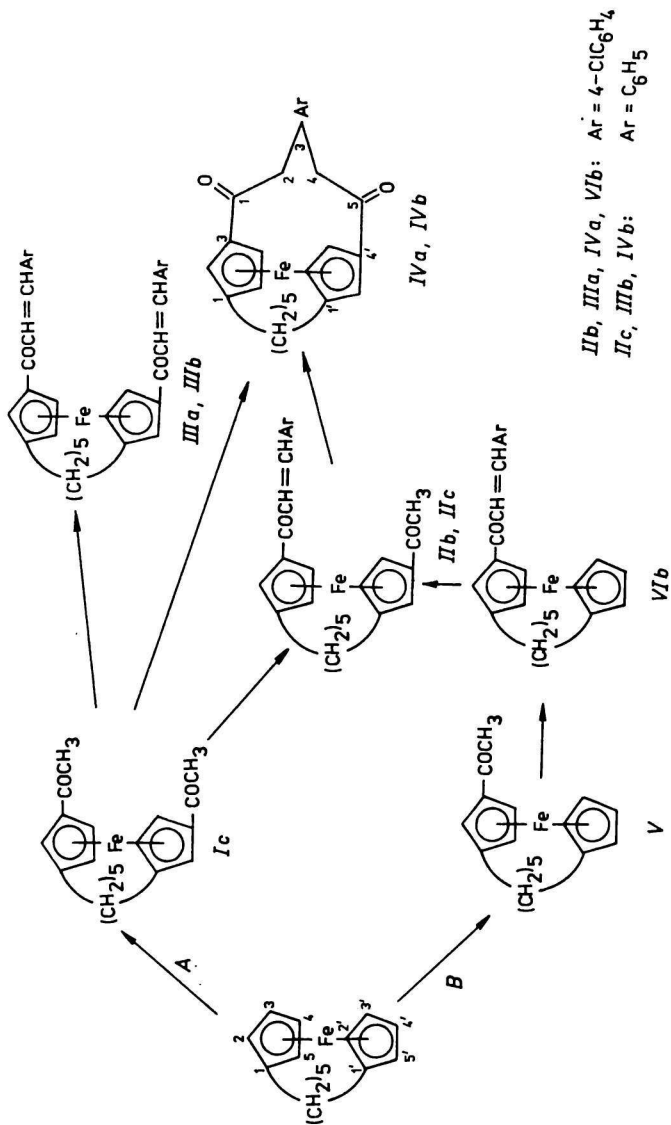
Scheme 1

spectrum of the dicinnamoyl derivative *IIIa* resembled that of *Ic* in the region of ferrocene proton shifts, whereas the spectrum of *IIb* showed two nonequivalent substituted cyclopentadienyl rings.

Since *Nesmeyanov et al.* [8] described an unsuccessful experiment to synthesize a derivative of [5](1,1')[5](3,4')ferrocenophane starting from 3,4'-diacetyl[5]ferrocenophane and benzaldehyde, we wanted to verify whether the substitution at benzaldehyde can cause an alteration in the reaction products composition. The reaction of the already mentioned components in boiling ethanolic sodium hydroxide afforded 3-phenyl[5](1,1')[5](3,4')ferrocenophane-1,5-dione (*IVb*), as well.

The second route (*B*) started from 3-acetyl[5]ferrocenophane (*V*), the structure of which was corroborated [9]. Condensation with 4-chlorobenzaldehyde led to 3-(4-chlorocinnamoyl)[5]ferrocenophane (*VI*). Its acetylation furnished two acetylated products *IIa*, *IIb*, which were separated by chromatography. The ^{1}H-n.m.r. spectrum of *IIa* displayed a doublet-doublet of the —CH=CH—CO group at $\delta = 7.74$ and 7.03 (2H), $J_{AB} = 15.6$ Hz, another doublet-doublet of aromatic protons at $\delta = 7.56$ and 7.38 (2H), $J_{AB} = 8.8$ Hz. Two multiplets were seen in the region of ferrocene proton shifts at $\delta = 4.81$ (m, 1H) and 4.58 (m, 2H), belonging to protons of β-substituted ring and one multiplet at $\delta = 4.25$ (m, 3H), belonging to protons of α-substituted ring. The singlet of COCH$_3$ group appeared at $\delta = 2.24$ (s, 3H) and protons of methylene groups had chemical shifts at $\delta = 2.4$ (m, 4H) and 2.85 (m, 6H). Basing upon this spectrum compound *IIa* was assigned the structure 2-acetyl-3'-(4-chlorocinnamoyl)- or 2-acetyl-4'-(4-chlorocinnamoyl)[5]ferrocenophane. It cannot be excluded that the mixture of both is involved.

The ^{1}H-n.m.r. spectrum of *IIb* showed the presence of a doublet-doublet of the —CH=CH—CO group at $\delta = 7.73$ and 7.03 (2H), $J_{AB} = 15.7$ Hz, and a doublet-doublet of aromatic protons at $\delta = 7.63$ and 7.39 (4H), $J_{AB} = 8.9$ Hz. Three multiplets were seen in the region of ferrocene proton shifts at $\delta = 4.65$ (1H), 4.54 (3H), and 4.44 (2H). The singlet of COCH$_3$ group at $\delta = 2.38$ (3H) was overlapped by a multiplet of two methylene groups of the bridge at $\delta = 2.35$ (4H); the remaining protons of methylene groups appeared as a multiplet at $\delta = 1.5$ (6H).

Treatment of 3-acetyl-4'-(4-chlorocinnamoyl)[5]ferrocenophane (*IIb*) with an ethanolic sodium hydroxide solution also afforded a doubly bridged ferrocene derivative *IVa*.

Experimental

The ^{1}H-n.m.r. (δ/p.p.m.) spectra of 10% and less deuteriochloroform solutions were measured with a Tesla BS 487 spectrometer operating at 80 MHz with tetramethylsilane as an internal standard. Melting points were determined on a Kofler micro hot-stage. Carriers

for chromatography were silica gel (Silpearl, Lachema, Brno) and aluminium oxide according to Brockmann (Reanal, Budapest, activity grade II). 3-Acetyl[5]ferrocenophane (*V*) was prepared by acetylation of [5]ferrocenophane according to [9].

Reaction of 3,4'-diacetyl[5]ferrocenophane (Ic) with 4-chlorobenzaldehyde

Method A

Aqueous sodium hydroxide (10%, 3 ml) was added with stirring to a solution of 3,4'-diacetyl[5]ferrocenophane (*Ic*) (0.34 g; 1 mmol) and 4-chlorobenzaldehyde (0.14 g; 1 mmol) in ethanol (20 ml). Stirring was continued for 24 h, the mixture was poured into water and extracted with dichloromethane. The extract was dried with Na_2SO_4, the solvent removed and the residue chromatographed on a silica gel column with benzene as eluent. Two products were isolated:

3,4'-Bis(4-chlorocinnamoyl)[5]ferrocenophane (*IIIa*) (0.2 g, 33%), m.p. 235—236°C (benzene).

For $C_{33}H_{28}Cl_2FeO_2$ (583.3) calculated: 9.57% Fe, 12.15% Cl; found: 9.59% Fe, 11.40% Cl. ^{1}H-NMR: 7.02 (d, 1H, —COCH=), 7.65 (d, 1H, $J_{AB} = 15.7$ Hz, =CH—), 7.44 and 7.20 (dd, 4H, $J_{AB} = 8.3$ Hz, C_6H_4), 4.74 (m, 2H) and 4.58 (m, 4H, C_5H_3), 2.36 (m, 4H, Fc—CH_2), 1.90 (m, 6H, CH_2). UV (λ_{max}): 305 nm (saturated methanolic solution).

3-Acetyl-4'-(4-chlorocinnamoyl)[5]ferrocenophane (*IIb*) (0.1 g, 21.2%), m.p. 159—160°C (acetone—light petroleum).

For $C_{26}H_{25}ClFeO_2$ (460.8) calculated: 12.12% Fe, 7.69% Cl; found: 12.40% Fe, 7.42% Cl. ^{1}H-NMR: 7.03 (d, 1H, —COCH=), 7.73 (d, 1H, $J_{AB} = 15.7$ Hz, =CH—), 7.63 and 7.39 (dd, 4H, $J_{AB} = 8.9$ Hz, C_6H_4), 4.65 (m, 1H), 5.54 (m, 3H), and 4.44 (m, 2H, C_5H_3), 2.38 (s, 3H, $COCH_3$), 2.35 (m, 4H, Fc—CH_2), 1.9 (m, 6H, CH_2). UV (λ_{max}): 316 nm (saturated methanolic solution).

Method B

Aqueous sodium hydroxide (10%, 3 ml) was added to a boiling solution of 3,4'-diacetyl[5] ferrocenophane (*Ic*) (0.34 g; 1 mmol) and 4-chlorobenzaldehyde (0.14 g; 1 mmol) in ethanol (20 ml) and heated for 2 h. After a 5 min boiling a precipitate began to separate; it was filtered off after cooling and thoroughly washed with acetone. Yield 0.15 g (32%) of 3-(4-chlorophenyl)[5](1,1')[5](3,4')ferrocenophane-1,5-dione (*IVa*), m.p. >260°C (decomposition).

For $C_{26}H_{25}ClFeO_2$ (460.8) calculated: 12.12% Fe, 7.69% Cl; found: 12.13% Fe, 7.52% Cl. ^{1}H-NMR: 7.3 (m, 4H, C_6H_4), 4.75 (m, 2H), 4.65 (m, 2H), and 4.44 (m, 3H, C_5H_3 + C<u>H</u>—Ph), 2.83 (dd, 2H, $J_{AB} = J_{AC} \doteq 12$ Hz, —$COCH_2$), 2.4 (m, 6H, —$COCH_2$ + Fc—CH_2), 1.95 (m, 6H, —CH_2—). UV (λ_{max}): 293 nm (saturated methanolic solution. MS (m/z): 460 (M^+).

The filtrate was extracted with dichloromethane, dried with Na_2SO_4 and the evaporated organic layer was chromatographed on silica gel with benzene as eluent. Yield: 3-acetyl-4'-(4-chlorocinnamoyl)[5]ferrocenophane (*IIb*) (20 mg, 4.2%) and the starting *Ic* (0.1 g, 29%).

Cyclization of 3-acetyl-4'-(4-chlorocinnamoyl)[5]ferrocenophane (IIb)

A solution of 3-acetyl-4-(4'-chlorocinnamoyl)[5]ferrocenophane (IIb) (0.23 g; 0.5 mmol) and sodium hydroxide (0.1 g) in ethanol (25 ml) was refluxed for 1 h. The mixture with a precipitate, which separated during heating, was poured into water and extracted with dichloromethane. The organic layer was dried with Na_2SO_4, distilled off and the residue chromatographed on a silica gel column with benzene—ethyl acetate 19 : 1 to give successively 3-(4-chlorophenyl)[5](1,1')[5](3,4')ferrocenophane-1,5-dione (IVa) (0.1 g, 43.4%), 3,4'-bis(4-chlorocinnamoyl)[5]ferrocenophane (IIIa) (60 mg, 21.4%), and the starting IIb (40 mg, 17.3%).

Reaction of 3,4'-diacetyl[5]ferrocenophane (Ic) with benzaldehyde

Aqueous sodium hydroxide (10%, 6 ml) was added to a boiling solution of 3,4'-diacetyl[5]ferrocenophane (Ic) (0.68 g; 2 mmol) and benzaldehyde (0.2 g; 2 mmol) in ethanol (40 ml) and the heating was continued for 2 h. The mixture was then poured into cold water, extracted with dichloromethane, which was dried with Na_2SO_4, distilled off and the residue was chromatographed on silica gel with benzene—ethyl acetate 19 : 1. Following products were isolated:

3-Phenyl[5](1,1')[5](3,4')ferrocenophane-1,5-dione (IVb) (0.2 g, 23.5%), m.p. 231—232°C (benzene).

For $C_{26}H_{26}FeO_2$ (426.3) calculated: 73.25% C, 6.14% H, 13.10% Fe; found: 73.38% C, 6.35% H, 13.29% Fe. ¹H-NMR: 7.7—7.2 (m, 5H, C_6H_5), 4.88 (m, 2H), 4.55 (m, 3H), and 4.43 (m, 1H, C_5H_3), 4.25 (m, 1H, CH—Ph), 3.25 (m, 2H, —COCH₂), 2.29 (m, 6H, —COCH₂ + Fc—CH₂), 1.75 (m, 6H, —CH₂—).

3,4'-Dicinnamoyl[5]ferrocenophane (IIIb) (30 mg, 3%), m.p. 135—137°C (acetone—hexane).

For $C_{33}H_{30}FeO_2$ (514.4) calculated: 77.04% C, 5.87% H, 10.25% Fe; found: 76.93% C, 6.03% H, 10.28% Fe. ¹H-NMR: 7.07 (d, 1H, —COCH=), 7.80 (d, 1H, J_{AAB} = 15.5 Hz, =CH—), 7.56 (m, 4H) and 7.28 (m, 6H, C_6H_5), 4.74 (m, 2H) and 4.58 (m, 4H, C_5H_3), 2.36 (m, 4H, Fc—CH₂), 1.90 (m, 6H, —CH₂—).

3-Acetyl-4'-cinnamoyl[5]ferrocenophane (IIc) (0.11 g, 13%), m.p. 149—151°C (acetone—hexane).

For $C_{26}H_{26}FeO_2$ (426.3) calculated: 73.25% C, 6.14% H, 13.10% Fe; found: 73.37% C, 6.30% H, 13.25% Fe. ¹H-NMR: 7.11 (d, 1H, —COCH=), 7.72 (d, 1H, =CH—), 7.69 (m, 2H) and 7.41 (m, 3H, C_6H_5), 4.65 (m, 1H), 4.54 (m, 3H), and 4.44 (m, 2H, C_5H_3), 2.34 (s, 3H, —COCH₃), 2.34 (m, 4H, Fc—CH₂), 1.90 (m, 6H, —CH₂—).

3-(4-Chlorocinnamoyl)[5]ferrocenophane (VIb)

Method A

Sodium hydroxide (0.2 g) dissolved in ethanol (10 ml) and water (5 ml) was dropwise added at room temperature to 3-acetyl[5]ferrocenophane (V) (1.5 g; 5 mmol) and

4-chlorobenzaldehyde (0.7 g; 5 mmol) dissolved in ethanol (30 ml). The mixture was stirred for 4 h, poured into water, extracted with dichloromethane and worked up as before. Yield 1 g (46.3%), m.p. 183—185°C (acetone—light petroleum).

For $C_{24}H_{23}ClFeO$ (418.7) calculated: 68.84% C, 5.53% H, 8.48% Cl, 13.33% Fe; found: 68.63% C, 5.28% H, 8.59% Cl, 13.65% Fe. ^1H-NMR: 7.03 (d, 1H, —COCH=), 7.70 (d, 1H, J_{AB} = 15.9 Hz, —CH=), 7.55 and 7.37 (dd, 4H, J_{AB} = 8.5 Hz, C_6H_4), 4.81(m, 1H), 4.72 (m, 1H), and 4.39 (m, 1H, C_5H_3), 4.19 (m, 2H) and 3.91 (m, 2H, C_5H_4), 2.30 (m, 4H, Fc—CH_2), 1.90 (m, 6H, —CH_2—).

Method B

A mixture consisting of 4-chlorocinnamic acid (1.82 g; 10 mmol) and phosphorous chloride (1.35 g; 10 mmol) in benzene (50 ml) was heated to 70°C for 2 h. Benzene was decanted, removed under diminished pressure and the residue (4-chlorocinnamoyl chloride) dissolved in anhydrous ether (50 ml). Aluminium chloride (3 g; 0.22 mol) was gradually added to the water-cooled ethereal solution to which [5]ferrocenophane (3.5 g; 13 mmol) in dry ether (100 ml) was added with stirring which was continued for 4 h. The mixture was poured onto crushed ice and extracted with dichloromethane. The usual work-up and chromatographic separation on alumina (eluent benzene) afforded in addition to the starting [5]ferrocenophane (2.48 g, 71%):

2-(4-Chlorocinnamoyl)[5]ferrocenophane (*VIa*) (0.55 g, 10%), m.p. 135—137°C (acetone—light petroleum).

For $C_{24}H_{23}ClFeO$ (418.7) calculated: 68.84% C, 5.53% H, 8.48% Cl, 13.33% Fe; found: 68.59% C, 5.37% H, 8.57% Cl, 13.61% Fe. ^1H-NMR: 7.08 (d, 1H, —COCH=), 7.65 (d, 1H, J_{AB} = 16 Hz, —CH=), 7.60 and 7.41 (dd, 4H, J_{AB} = 8.4 Hz, C_6H_4), 4.71 (m, 1H), 4.49 (m, 1H), and 4.45 (m, 1H, C_5H_3), 4.36 (m, 1H), 4.24 (m, 1H), 3.89 (m, 1H), and 3.82 (m, 1H, C_5H_4), 2.30 (m, 4H, Fc—CH_2—), 1.85 (m, 6H, —CH_2=).

3-(4-Chlorocinnamoyl)[5]ferrocenophane (*VIb*) (1.1 g, 19%), m.p. 183—185°C (acetone—light petroleum).

3-(4-Chlorophenyl)[5](1,1')[5](3,4')ferrocenophane-1,5-dione (IVa)

Ethanol (30 ml) was added to a solution of *IIIa* (0.3 g; 0.5 mmol) in tetrahydrofuran (20 ml), the latter was distilled off and aqueous sodium hydroxide (10%, 5 ml) was dropwise added at the boiling temperature. The mixture, from which a precipitate began to separate after 5 min, was heated for 4 h, cooled, poured into water, extracted with dichloromethane and worked up as above (carrier alumina, eluent dichloromethane). Yield 0.12 g (52%), m.p. >260°C (decomposition).

Acetylation of [5]ferrocenophane

A solution of [5]ferrocenophane (2.5 g; 10 mmol) and acetyl chloride (2.3 g; 30 mmol) in dichloromethane (30 ml) was dropwise added during 1 h to aluminium chloride (4 g; 30 mmol) in dichloromethane (30 ml) at room temperature. The boiling mixture was stirred

for additional 1 h, cooled, poured onto crushed ice and extracted with dichloromethane. The usual work-up followed by chromatography on alumina with benzene as an eluent afforded in addition to the unreacted [5]ferrocenophane (1.1 g, 44%):

3-Acetyl[5]ferrocenophane (*V*) (0.15 g, 5%), m.p. 65—68°C (light petroleum); Ref. [9] gives m.p. 66—68°C.

Unresolvable mixture of isomeric 2,3'-diacetyl[5]ferrocenophane (*Ia*) and 2,4'-diacetyl[5]ferrocenophane (*Ib*) (0.65 g, 22%), m.p. 93—97°C (acetone—light petroleum).

For $C_{19}H_{22}FeO_2$ (338.2) calculated: 67.48% C, 6.56% H, 16.51% Fe; found: 67.56% C, 6.87% H, 16.35% Fe. ^{1}H-NMR: 4.65 (m, 1H), 4.57 (m, 1H), and 4.44 (m, 1H, β-substituted ring C_5H_3), 4.25 (m, 3H, α-substituted ring C_5H_3), 2.31 (s, 3H, α-COCH_3), 2.40 (s, 3H, β-COCH_3).

3,4'-Diacetyl[5]ferrocenophane (*Ic*) (0.55 g, 19%), m.p. 126—127.5°C (acetone—light petroleum); Ref. [8] gives m.p. 126—127°C. ^{1}H-NMR: 4.54 (m, 2H) and 4.44 (m, 4H, C_5H_3), 2.38 (s, 6H, —COCH_3), 2.38 (m, 4H, Fc—CH_2), 1.90 (m, 6H, —CH_2—).

Acetylation of 3-(4-chlorocinnamoyl)[5]ferrocenophane (VIb)

Aluminium chloride (1.6 g; 12 mmol) was successively added with stirring to 3-(4-chlorocinnamoyl)[5]ferrocenophane (1.6 g; 4 mmol) and acetyl chloride (0.64 g; 8 mmol) in dichloromethane (60 ml) at room temperature. The mixture was stirred for 5 h, poured onto ice, extracted with dichloromethane and worked up. Chromatographic separation on silica gel with benzene as eluent showed 7 bands; the second and the fifth of which afforded a very small amount of the respective substances so that the identification was impossible. The first band contained *VIb* (0.7 g, 44%), the third gave 2-acetyl-3'(4')-(4-chlorocinnamoyl)[5]ferrocenophane (*IIa*) (0.18 g, 10%), m.p. 142—143°C (acetone—light petroleum).

For $C_{26}H_{25}ClFeO_2$ (460.8) calculated: 7.69% Cl, 12.12% Fe; found: 8.00% Cl, 12.10% Fe. ^{1}H-NMR: 7.03 (d, 1H, —COCH=), 7.74 (d, 1H, $J_{AB}=15.6$ Hz, —CH=), 7.56 and 7.38 (dd, 4H, $J_{AB}=8.8$ Hz, C_6H_4), 4.83 (m, 1H) and 4.58 (m, 2H, β-substituted C_5H_3), 4.25 (m, 3H, α-substituted C_5H_3), 2.24 (s, 3H, —COCH_3), 2.40 (m, 4H, Fc—CH_2=), 1.85 (m, 6H, —CH_2—). The fourth band yielded 3-acetyl-4'-(4-chlorocinnamoyl)[5]ferrocenophane (*IIb*) (0.21 g, 12%), m.p. 159—160°C (acetone—light petroleum, identical with that obtained by condensation of 3,4'-diacetyl[5]ferrocenophane and 4-chlorobenzaldehyde), the sixth band furnished a yellow compound (90 mg) which did not melt up to 300°C (dichloromethane), and the seventh band afforded a yellow compound (m.p. 285—290°C — acetone).

References

1. Hisatome, M., Sakamoto, T., and Yamakawa, K., *J. Organometal. Chem. 107,* 87 (1976).
2. Furdík, M., Toma, Š., Suchý, J., and Elečko, P., *Chem. Zvesti 15,* 45 (1961).
3. Masburn, T. A., Jr., Cain, C. E., and Hauser, C. R., *J. Org. Chem. 25,* 1982 (1960).
4. Furdík, M., Elečko, P., and Kováč, Š., *Chem. Zvesti 21,* 501 (1967).
5. Barr, T. H. and Watts, W. E., *Tetrahedron 24,* 3219 (1968).
6. Elečko, P., *Chem. Zvesti 23,* 198 (1969).
7. Livař, M., Sališová, M., and Toma, Š., *Collect. Czech. Chem. Commun. 40,* 415 (1975).
8. Nesmeyanov, A. N., Rybinskaya, M. I., Shulpin, G. B., and Tolstaya, M. V., *Dokl. Akad. Nauk SSSR 229,* 1124 (1976).
9. Barr, T. H., Bolton, E. S., Lentzner, H. L., and Watts, W. E., *Tetrahedron 25,* 5243 (1969).