STUDY OF THE REACTIVITY OF 2-BENZYLIDENE[3]FERROCENOPHANE-1,3-DIONE WITH ETHYL ACETOACETATE AND SOME OTHER C-NUCLEOPHILES

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Received July 2, 1992
Accepted May 24, 1993

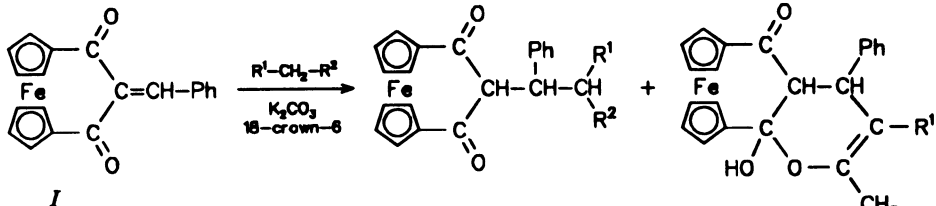
Michael addition of C-nucleophiles to 2-benzylidene[3]ferrocenophane-1,3-dione has been studied. In some cases, (ethyl acetoacetate, acetylacetone and malononitrile as the C-nucleophiles) the addition was followed by intramolecular cyclization leading to pyran derivatives. Addition of malononitrile gave the pyran derivative as the sole product. The Michael adducts of ethyl acetoacetate and acetylacetone can be converted to [7]ferrocenophane-1,7-dione derivatives by refluxing in benzene with triethylamine as catalyst. They also easily react with ammonia, under SiO_2 catalysis, to give Hantzsch dihydropyridine derivatives. The ^1H NMR spectra of the products are discussed.

Michael addition of different C-nucleophiles to 2-(3-chlorobenzylidene)[3]ferrocenophane-1,3-dione has been described[1,2]. In most cases the real Michael adducts have not been isolated but the bridge enlargement was observed and derivatives of [7]ferrocenophane-1,7-dione were obtained. When ethyl acetoacetate was used as the nucleophile, the only product, which was only partially characterized, was a dihydropyridine derivative. It was suggested that the nitrogen atom was incorporated into the product during column chromatography on SiO_2 silica gel, containing some residual ammonia from its manufacture.

The main goal of this work was to study the Michael addition of similar C-nucleophiles to 2-benzylidene[3]ferrocenophane-1,3-dione with the hope that the products will be more soluble, and therefore can be more precisely characterized. The second goal of this work was to get some insight into the mechanism of formation of the dihydropyridine derivative and to prove its structure.

RESULTS AND DISCUSSION

Michael addition of various C-nucleophiles to 2-benzylidene[3]ferrocenophane-1,3-dione *I* was carried out in benzene using the system K_2CO_3/18-crown-6 as catalyst. The reactions proceeded smoothly at room temperature (Scheme 1).



I

IIa, R^1 = $COOC_2H_5$; R^2 = $COCH_3$
IIIa, R^1 = R^2 = $COCH_3$
IV, R^1 = R^2 = $COOCH_3$
V, R^1 = $COOC_2H_5$; R^2 = CN
VI, R^1 = $COOCH_3$; R^2 = CN
VII, R^1, R^2 = $CO(CH_2)_3CO$

IIb, R^1 = $COOC_2H_5$
IIIb, R^1 = $COCH_3$

SCHEME 1

The reaction with ethyl acetoacetate yielded a yellow material, consisting of two substances, according to TLC. Attempts to separate them by chromatography on SiO_2 column failed and, instead of separation, a third, nitrogen containing compound was detected and isolated. Analogous results were described previously[1,2]. On the other hand, successful separation was achieved on a Silpearl (Kavalier, Votice) column and the thus-obtained compounds *IIa* and *IIb* were isolated and investigated.

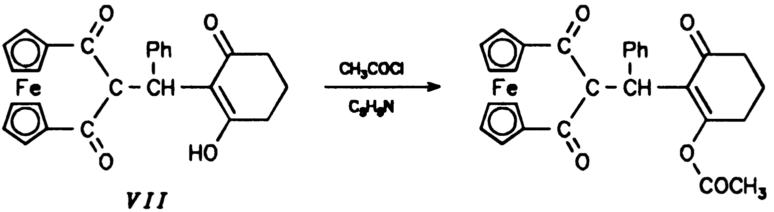
^{1}H NMR spectrum of *IIa* was rather complicated and two different signals of $COCH_3$ as well as OCH_2CH_3 groups were observed in a ratio close to 1 : 1. We assume therefore that the compound *IIa* is a mixture of two diastereoisomers of ethyl 2-acetyl-3-(1,3-dioxo[3]ferrocenophane-2-yl)-3-phenylpropionate. Attempts to separate them either by chromatography or crystallization were unsuccessful. In the best case, the crystallization gave a 4 : 1 mixture of diastereoisomers.

Compound *IIb* was invariably contaminated (TLC) by various amounts of *IIa* and all purification attempts failed due to its easy isomerization to *IIa*. Nevertheless, it was possible to distinguish two doublets for CH-Ph in the ^{1}H NMR spectrum as well as pyran protons at δ 3.05 and 3.20 (d, ^3J(H,H) = 14.4 and 9.3, respectively). Two singlets of $=C-CH_3$ protons at δ 1.59 and 1.65 were also observed. Analogous ^{1}H NMR spectrum was taken for *IIIb* as well (see below). Compound *IIb* consisted of two (cis-trans) isomers.

Michael addition of acetylacetone to *I* resulted also in two compounds *IIIa* and *IIIb* which were separated by chromatography on Silpearl column. The isomerization of *IIIb* → *IIIa* is much slower than *IIb* → *IIa*, and *IIIb* was therefore isolated in pure state. Its ^{1}H NMR and IR spectra proved that *IIIb* is a hydroxy derivative of 4*H*-pyran which was formed by cyclization of an enol form of *IIIa*. Similar structures were already described[3,4]. It is of interest to note that *IIIb* is again a mixture of two geometrical isomers but, according to the ^{1}H NMR spectrum, they differ considerably in thermodynamic stability. The ratio of the respective signals in the spectra of *IIIa* and *IIIb* (for $=C-CH_3$ (s, 3 H) at δ 1.52 and 1.56, for $COCH_3$ (s, 3 H) at δ 1.88 and 2.00 and for CH–Ph at δ 3.27 and 3.33 (d, 1 H, $^3J(H,H)$ = 11.4 and 9.6 Hz)) was found to be close to 4 : 1.

The addition of dimethyl malonate, ethyl cyanoacetate, methyl cyanoacetate and 1,3-cyclohexanedione proceeded smoothly and only a single product (*IV* – *VII*; Scheme 1) was isolated in each case. Examining ^{1}H NMR spectra of the compounds *V* and *VI* we were surprised that only one signal of OCH_2CH_3 or OCH_3 groups was observed in spite of the fact that two diastereoisomers should had been formed. We assume that the 300 MHz NMR instrument used was not sensitive enough to distinguish small differences in chemical shifts of these diastereoisomers. On the other hand, it is not surprising that two signals of $COCH_3$ in *IIIa* as well as of $COOCH_3$ in *IV* were found because the compounds contain prochiral centres $CH(COCH_3)_2$ and $CH(COOCH_3)_2$, respectively.

Having in hand the ^{1}H NMR spectra of all compounds *IIa* – *VII*, we could unambiguously assign the chemical shifts of CO–CH–CO as well as CH–COOR protons. Since the 1,3-cyclohexanedione adduct *VII* was very insoluble, we prepared the acetyl derivative *VIII* (Scheme 2) which was reasonably soluble and afforded a very good ^{1}H NMR spectrum confirming the structure *VIII*.

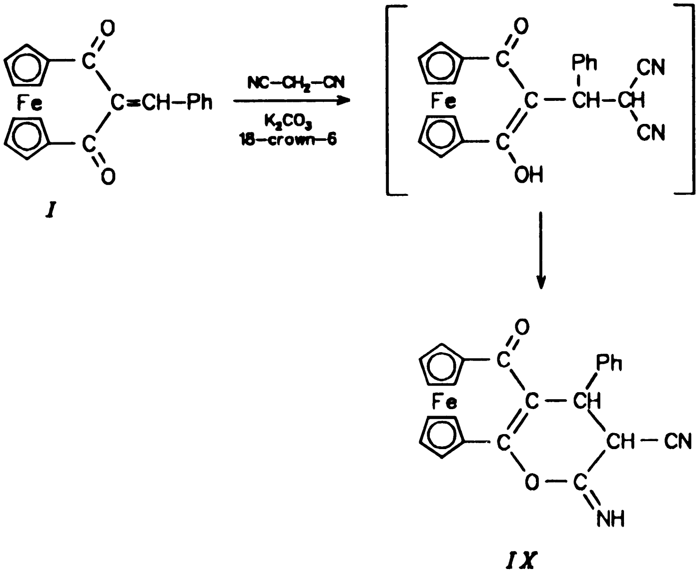


VII

VIII

SCHEME 2

In all the cases discussed above, the Michael addition of various C-nucleophiles to 2-benzylidene[3]ferrocenophane-1,3-dione *I* under K_2CO_3/18-crown-6 catalysis yielded the normal Michael adducts as the main products. Addition of malononitrile under the same conditions yielded a different product. The Michael adduct was merely the intermediate, but the only isolated product was the iminopyran derivative *IX* (Scheme 3).

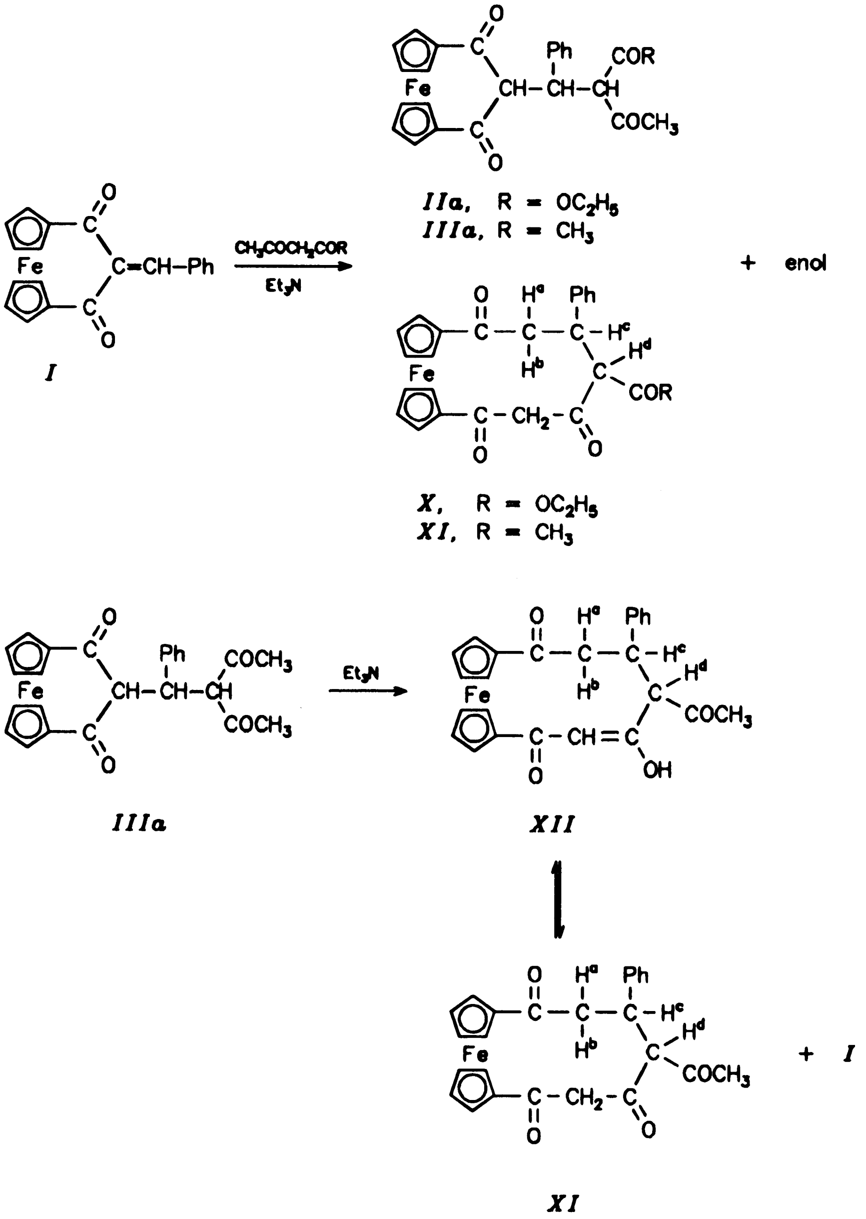


SCHEME 3

Its ^{1}H NMR spectrum was of no use for the structure elucidation as all proton signals were found in a very narrow region. The structure assignment of *IX* is based on ^{13}C NMR spectrum where two signals for sp^3 carbon were identified: one at δ 40.10 (CH–Ph) and a second at δ 61.79 (CH–CN). The formation of 4*H*-pyran skeleton in the addition of malononitrile to α-enones was observed[3,6 – 10], but usually such products had an amino and not an imino structure. We can speculate that under our very mild conditions Dimroth rearrangement[8 – 12] did not take place.

As mentioned earlier, Michael addition of different C-nucleophiles to 2-(3-chlorobenzylidene)[3]ferrocenophane-1,3-dione in refluxing benzene resulted in bridge-enlargement products. It was therefore of interest to investigate the reaction products with 2-benzylidene[3]ferrocenophane-1,3-dione *I*, if the reaction is carried out under the conditions described earlier[2]. Acetylacetone and ethyl acetoacetate were chosen as the reagents and the results are depicted in Scheme 4.

In both cases, the normal Michael adducts *IIa* and *IIIa* as well as the bridge enlargement products *X* and *XI* were isolated. The structure of *X* and *XI* was proved by ^{1}H NMR spectra that were similar to those for the [7]ferrocenophane-1,7-dione derivatives described earlier[2]. The fact that the [3]ferrocenophane-1,3-dione derivative *IIIa* is an intermediate on the reaction path to the [7]ferrocenophane-1,7-dione derivative *XI*

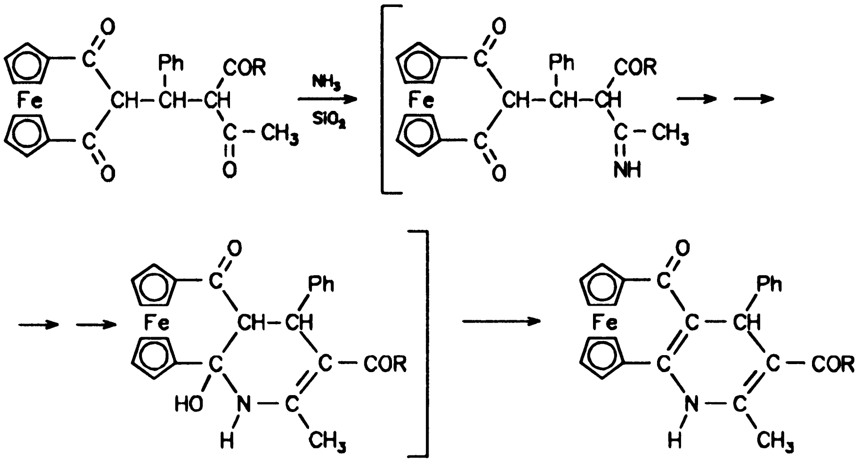

I
IIa, R = OC2H5
IIIa, R = CH3
X, R = OC2H5
XI, R = CH3
CH3COCH2COR
Et3N
+ enol
IIIa
XII
XI
+ I

SCHEME 4

was proved by an independent experiment. Refluxing of *IIIa* in benzene with triethylamine resulted in the bridge-enlargement product *XI* (60%) and its enol form *XII* (10% according to the ^{1}H NMR). Such stable enol form has not been described earlier. The starting material *I* (30%), which is the product of retro-Michael addition, was also isolated.

The fact that [7]ferrocenophane-1,7-dione derivatives *X* and *XI* are not the main reaction products may have a trivial explanation. The products resulting from the Michael addition to 2-(3-chlorobenzylidene)[3]ferrocenophane-1,3-dione are insoluble and crystallize from the reaction medium, shifting thus the equilibrium in favour of their formation.

Having solved the problem of Michael addition of different C-nucleophiles to 2-benzylidene[3]ferrocenophane-1,3-dione, we decided to investigate the formation of the nitrogen containing product, arising during chromatography of *IIa* on SiO_2. We designed the experiment in which NH_3 gas was passed through a solution of *IIa* in benzene. TLC indicated that a new compound having R_F in between those of *IIa* and *IIb* was formed, but the reaction was very slow. The rate of its formation, as well as its yields, increased substantially when SiO_2 was added to the reaction mixture. This rate enhancement is in accord with the observation that many reactions are accelerated in the presence of inorganic carriers like SiO_2, Al_2O_3 or montmorillonite[13-15]. Further on, we examined whether a similar product could be formed starting from *IIIa*. The result was positive (Scheme 5).



XIII, R = OCH_3

XIV, R = CH_3

SCHEME 5

The structure of the products *XIII* and *XIV* as the Hantzsch 1,4-dihydropyridine derivatives was proved by their ^{1}H NMR spectra (singlet at δ 6.11; diminished after D_2O addition), IR spectra (ν(NH) at 3 428 cm^{-1}) as well as ^{13}C NMR spectra (four signals for sp^2 carbons of dihydropyridine ring).

EXPERIMENTAL

2-Benzylidene[3]ferrocenophane-1,3-dione was prepared by the reported procedure[1]. All the C-nucleophiles were commercially available compounds, freshly distilled before use. Melting points were determined on a Kofler block, and are not corrected. ^{1}H NMR and ^{13}C NMR spectra (δ, ppm and *J*, Hz) were recorded on a Varian VXR (300 MHz) instrument in $CDCl_3$ with TMS as internal standard. IR spectra (ν, cm^{-1}) were taken on Specord M-80 spectrometer in $CHCl_3$ or in NUJOL. Flash column chromatography was performed on silica (Lachema, Brno; particle size 0.15 to 0.42 mm), or on Silpearl (Kavalier, Votice) in benzene–ethyl acetate mixtures.

Addition of C-Nucleophiles to 2-Benzylidene[3]ferrocenophane-1,3-dione under Phase-Transfer Conditions. General Procedure

The corresponding C-nucleophile (3 mmol) in anhydrous benzene (20 ml) was added to a stirred mixture of 2-benzylidene[3]ferrocenophane-1,3-dione *I* (2 mmol), 18-crown-6 (0.7 mmol), K_2CO_3 (0.5 g) and anhydrous benzene (50 ml) at room temperature. The colour of the solution changed from violet to orange-yellow. The reaction mixture was stirred for 0.5 – 4 h (until no starting material was present, or no change was observed by TLC). The products precipitated in some cases. K_2CO_3 was then removed and the solvent was evaporated on a rotary vacuum evaporator. The residue was chromatographed on silica or Silpearl in benzene containing 10 – 30% of ethyl acetate.

Addition of ethyl acetoacetate. Ethyl 2-acetyl-3-(1,3-dioxo[3]ferrocenophane-2-yl)-3-phenylpropanoate *IIa* was obtained from *I* and ethyl acetoacetate in 60% yield. The product was isolated by chromatography on Silpearl from the first fraction, m.p. 152 – 159 °C (benzene–hexane). For $C_{26}H_{24}FeO_5$ (472.3) calculated: 66.11% C, 5.12% H, 11.82% Fe; found: 66.70% C, 5.20% H, 11.25% Fe. ^{1}H NMR spectrum: 1.11 t and 1.17 t, 3 H (CH_3); 2.19 s and 2.22 s, 3 H (CH_3CO); 4.0 – 4.1 m, 1 H (CHCOO); and 4.05 q, 2 H (CH_2); 4.31, 4.86, 4.89, 5.13 and 5.26 m, 2 + 1/2 H (Fc); 4.4 – 4.6 m, 6 + 1/2 H (Fc and CHPh); 5.16 d, ^3J = 9.9 and 5.50 d, ^3J = 10.5, 1 H (CHCO); 7.15 – 7.45 m, 5 H (Ph). ^{13}C NMR spectrum: 13.84 (CH_3), 29.84 (CH_3CO), 41.23 (CHPh), 61.42 (CH_2), 63.01 (CHCOO), 69.53 (CHCO), 70.11, 73.10, 73.11, 73.16, 73.59, 74.03, 74.32, 74.59, 89.43 and 89.96 (Fc); 127.23, 128.43, 129.16 and 139.03 (Ph); 169.03 (COOR); 190.75 and 192.26 (COFc); 203.80 ($COCH_3$). IR spectrum ($CHCl_3$): 1 168, 1 272 (C–O); 1 670, 1 710 (C=O); 1 732 (CO–O).

The compound *IIb* was isolated from the second fraction (20 – 30%). The structure of *IIb* was not unambiguously proved due to its instability and decomposition during flash chromatography and was suggested only on the basis of ^{1}H NMR spectrum of the mixture of *IIa* and *IIb*.

Addition of acetylacetone. 3-[2-(1,3-Dioxo-[3]ferrocenophanyl)phenylmethyl]-2,4-pentanedione *IIIa* was obtained from *I* and acetylacetone in 60% yield. The starting 2-benzylidene[3]ferrocenophane-1,3-dione *I* (5%) was isolated by chromatography on Silpearl from the first fraction. The product *IIIa* was isolated from the second fraction m.p. 178 – 183 °C (benzene–hexane). As shown by elemental analysis and ^{1}H NMR spectra, it crystallized with one molecule of benzene. For $C_{25}H_{23}FeO_4 . C_6H_6$ (520.3) calculated: 71.70% C, 5.42% H; found: 70.32% C, 5.35% H. ^{1}H NMR spectrum: 2.09 s, 3 H (CH_3); 2.21 s, 3 H (CH_3); 4.23 m, 1 H (Fc); 4.39 d, ^3J(H,H) = 6.1, 1 H ($CHCOCH_3$); 4.41 m, 1 H (Fc); 4.45 m, 1 H (Fc); 4.49 m, 1 H, (Fc); 4.53 m, 2 H (Fc + CHPh); 4.57 m, 1 H (Fc); 4.83 m, 1 H (Fc); 5.13 m, 1 H (Fc); 5.14 d, ^3J(H,H) = 9.3, 1 H (CHCOFc); 7.15 –

7.40 m, 5 H (Ph). ^{13}C NMR spectrum: 30.56 and 30.90 (CH_3); 41.94 (CH–Ph); 69.69 and 69.80 (CHCO, $CHCOCH_3$); 70.20, 70.28, 73.20, 73.26, 73.78, 74.29, 74.81, 88.60 and 89.75 (Fc); 127.45, 128.34, 129.15 and 139.26 (Ph); 191.34 and 192.49 (CO); 204.94 and 205.19 ($COCH_3$). IR spectrum ($CHCl_3$): 1 192 (C–O); 1 280, 1 645, 1 695, 1 706 (C=O).

Compound *IIIb* was isolated from the third fraction (20%), m.p. 150 – 156 °C (benzene). For $C_{25}H_{23}FeO_4$ (442.3) calculated: 67.88% C, 5.01% H; found: 67.88% C, 5.01% H. ^{1}H NMR spectrum: 1.52 and 1.56 s, 3 H (=C–CH_3); 1.89 and 2.00 s, 3 H ($COCH_3$); 3.27 and 3.45 d, ^3J(H,H) = 11.4 and 9.7, 1 H (CH–Ph); 4.28 – 4.67 m, 10 H (CH–CO,OH,Fc); 7.15 – 7.40 m, 5 H, (Ph). IR spectrum (NUJOL): 1 230 (C–O); 1 575 (C=C); 1 600, 1 705 (C=O); 3 250 broad (OH).

Addition of dimethyl malonate. Dimethyl 2-[2-(1,3-dioxo[3]ferrocenophanyl)phenylmethyl]-malonate *IV* was obtained from *I* and dimethyl malonate in 95% yield. The starting 2-benzylidene[3]ferrocenophane-1,3-dione *I* (2 – 5%) was isolated by chromatography on silica from the first fraction. The product *IV* was isolated from the second fraction, m.p. 204 – 207 °C (benzene–hexane). For $C_{25}H_{22}FeO_6$ (474.4) calculated: 63.31% C, 4.67% H, 11.77% Fe; found: 63.46% C, 4.69% H, 11.75% Fe. ^{1}H NMR spectrum: 3.62 s and 3.67 s, 3 H (CH_3); 3.95 d, J = 6.3, 1 H (CHCOOR); 4.42 – 4.60 m, 7 H (Fc + CHPh); 4.93 m, 1 H (Fc); 5.24 m, 1 H (Fc) 5.52 d, ^3J(H,H) = 11.1, 1 H (CHCO); 7.15 – 7.40 m, 5 H (Ph). IR spectrum ($CHCl_3$): 1 168, 1 274 (C–O); 1 670, 1 706 (C=O); 1 728, 1 749 (CO–O).

Addition of ethyl cyanoacetate. Ethyl 2-cyano-3-[2-(1,3-dioxo[3]ferrocenophanyl)]-3-phenylpropanoate *V* was obtained from *I* and ethyl cyanoacetate in 88% yield. The product was isolated by chromatography on silica as a mixture of diastereoisomers, m.p. 185 – 194 °C (benzene–hexane). For $C_{35}H_{21}FeNO_4$ (455.3) calculated: 65.95% C, 4.65% H, 3.08% N, 12.27% Fe; found: 66.70% C, 4.67% H, 2.89% N, 11.98% Fe. ^{1}H NMR spectrum: 1.05 t, 3 H (CH_3); 4.00 q and 4.01 q, 2 H (CH_2); 4.34 d, ^3J(H,H) = 6 Hz, 1 H (CHCOOR); 4.45 – 4.65 m, 7 H (Fc + CHPh); 4.91 m, 1 H (Fc); 5.18 d, J = 11.4 Hz, 1 H (CHCO); 5.26 m, 1 H (Fc); 7.25 – 7.55 m, 5 H (Ph). ^{13}C NMR spectrum: 13.76 (CH_3); 40.78 and 41.03 (CHCN,CHPh); 62.67 (CH_2); 68.91 (CHCO); 69.53, 71.24, 73.09, 73.16, 73.32, 74.19, 74.53, 74.56, 90.69 and 90.82 (Fc); 116.11 (CN); 128.39, 128.52, 128.83 and 136.02 (Ph); 164.44 (COO); 188.47 and 191.91 (CO). IR spectrum (NUJOL): 1 196, 1 270 (C–O); 1 665, 1 698 (C=O); 1 735 (CO–O); 2 248 (CN).

Addition of methyl cyanoacetate. Methyl 2-cyano-3-(2-(1,3-dioxo[3]ferrocenophanyl))-3-phenylpropanoate *VI* was obtained from *I* and methyl cyanoacetate in 85% yield and purified by chromatography on silica as a mixture of diastereoisomers, m.p. 215 – 219 °C (decomp.) (benzene–hexane). For $C_{24}H_{19}FeNO_4$ (441.2) calculated: 65.32% C, 4.34% H, 3.17% N, 12.66% Fe; found: 65.68% C, 4.45% H, 2.67% N, 11.50% Fe. ^{1}H NMR spectrum: 3.57 s, 3 H (CH_3); 4.35 d, ^3J(H,H) = 5.7, 1 H (CHCOOR); 4.45 – 4.65 m, 7 H (Fc + CHPh); 4.93 m, 1 H (Fc); 5.18 d, ^3J(H,H) = 11.7, 1 H (CHCO); 5.26 m, 1 H (Fc); 7.25 – 7.50 m, 5 H (Ph). ^{13}C NMR spectrum: 40.82 and 41.07 (CHCOOR,CHPh); 53.23 (CH_3); 68.92 (CHCO); 69.95, 70.98, 73.11, 73.19, 73.30, 74.15, 74.58, 90.65 and 90.79 (Fc); 115.92 (CN); 128.34, 128.46, 128.93 and 135.96 (Ph); 164.94 (COOR); 188.40 and 191.92 (CO); IR spectrum (NUJOL): 1 170, 1 252 (C–O); 1 640, 1 690 (C=O); 1 740 (CO–O); 2 235 (CN).

Addition of 1,3-cyclohexanedione. 2-(2,4-Dioxohexylphenylmethyl)[3]ferrocenophane-1,3-dione *VII* was obtained from *I* and 1,3-cyclohexanedione after stirring for 1 h. No starting 2-benzylidene[3]ferrocenophane-1,3-dione *I* was present (TLC). The insoluble yellow product was filtered off and washed with ether (or dichloromethane) to remove excess of 1,3-cyclohexanedione and the rest of 18-crown-6. The product was separated from K_2CO_3 by extraction with refluxing ethanol and compound *VII* was isolated in an almost quantitative yield. It did not melt up to 360 °C (ethanol). For $C_{26}H_{22}FeO_4$ (454.3) calculated: 68.73% C, 4.88% H; found: 68.46% C, 5.05% H. IR spectrum (NUJOL): 1 596 (C=C); 1 614, 1 670 (C=O); 3 102 (OH).

Acetyl chloride (0.5 ml) in chloroform (3 ml) was added to a solution of *VII* and triethylamine (0.5 ml) (0.25 mmol) in anhydrous chloroform (7 ml). After stirring for 2 h, the reaction mixture was poured at 0 °C into dilute (1 : 1) HCl (10 ml). The organic layer was separated, washed with water and dried over anhydrous Na_2SO_4. Sodium sulfate was filtered off and the solvent was evaporated. The residue was chromatographed on a Silpearl column with benzene–ethyl acetate as eluent. From the first fraction 2-(2-acetyloxy-6-oxo-1-cyclohexylphenylmethyl)[3]ferrocenophane-1,3-dione (*VIII*), m.p. 190 – 195 °C (benzene–hexane), was isolated in almost quantitative yield. For $C_{28}H_{24}FeO_5$ (496.3) calculated: 67.75% C, 4.87% H; found: 67.82% C, 4.97% H. ^1H NMR spectrum: 1.94 m, 2 H (CH_2);, 2.35 s, 3 H (CH_3); 2.37 t, 2 H, (CH_2C=); 2.65 dd, 2 H (CH_2CO), 4.40 m, 2 H (Fc); 4.49 m, 2 H (Fc); 4.52 m, 2 H (Fc); 4.93 m, 1 H (Fc); 5.06 d, $^3J(H,H)$ = 11.4, 1 H (CHCO); 7.1 – 7.4 m, 5 H (Ph). ^{13}C NMR spectrum: 20.85 and 21.22 (CH_3); 29.19 (CH_2); 38.42 and 38.64 (CH_2C=, CH_2CO); 68.76, 68.92, 71.01, 72.37, 72.40, 73.34, 73.75, 73.82, 74.25, 91.17 and 91.48 (CHCO, Fc); 126.62, 128.41, 128.47 and 128.49 (Ph); 141.24 (=CCH_2); 168.07 and 167.58 (=CCO, COOR); 192.06 and 192.2 (COFc); 201.08 (CO). IR spectrum (NUJOL): 1 155, 1 197, 1 295 (C–O); 1 605, 1 653, 1 698 (CO); 1 766 (CO–O).

Addition of malononitrile. The 4*H*-pyran derivative *IX* was obtained from *I* and malononitrile in 72% yield. The unreacted 2-benzylidene[3]ferrocenophane-1,3-dione *I* (15%) was isolated by chromatography on silica from the first fraction. The product *IX* was isolated from the second fraction, m.p. 221 – 227 °C (benzene–cyclohexane). For $C_{24}H_{16}FeN_2O_2$ (408.3) calculated; 67.66% C, 3.95% H, 6.85% N, 13.68% Fe; found: 67.90% C, 3.95% H, 6.59% N, 13.58% Fe. ^1H NMR spectrum: 4.26 m, 1 H (CHPh); 4.38 m, 2 H (Fc); 4.40 m, 2 H (Fc); 4.45 bs, 1 H, (CHCN); 4.54 m, 2 H (Fc); 4.63 m, 1 H (Fc); 4.65 m, 1 H (Fc); 4.79 s, 1 H (NH); 7.2 – 7.4 m, 5 H (Ph). ^{13}C NMR spectrum: 40.10 (CHPh); 61.79 (CHCN); 71.73, 72.92, 72.97, 73.25, 73.37, 73.51, 73.85, 74.36, 77.22 and 85.72 (Fc); 118.75 (=C–CO); 123.04 (CN); 127.51, 127.88, 128.85 and 143.03 (Ph); 151.84 (=C–O); 157.94 (O–C=NH); 193.37 (CO). IR spectrum ($CHCl_3$): 1 632 (C=C); 1 642 (C=NH); 1 672 (CO); 2 200 (CN); 3 404 (NH).

Addition of C-Nucleophiles to 2-Benzylidene[3]ferrocenophane-1,3-dione *I* under Et_3N Catalysis

Addition of ethyl acetoacetate. Ethyl acetoacetate (5 mmol) and triethylamine (1.5 ml) were added to a solution of 2-benzylidene[3]ferrocenophane-1,3-dione (1.3 mmol) *I* in anhydrous benzene (100 ml). The reaction mixture was heated to reflux for 7 h and then left to stand overnight. The solvent was evaporated on a rotary evaporator, the residue was dissolved in benzene and the solvent was evaporated once again. The crude reaction mixture was dissolved in hot benzene (about 100 ml). Small amount of crystalline *X* was filtered off after cooling and the residue was chromatographed on Silpearl. The compound *IIa* (60%) was isolated from the first fraction, m.p. 150 – 155 °C. The minor products from the second and the third fraction were not identified. Yellow 4-ethoxycarbonyl-4-hydroxy-5-phenyl[7]ferrocenophane-2-ene-1,7-dione (*X*) (10%) was isolated from the fourth fraction, m.p. 210 – 223 °C (benzene). For $C_{26}H_{24}FeO_5$ (472.3) calculated: 66.19% C, 5.12% H; found: 65.57% C, 5.16% H. ^1H NMR spectrum: 1.08 t, 3 H (CH_3); 2.72 d, 1 H (CH_2); 2.94 d, 1 H (CH_2); 3.38 s, 1 H ($COCH_2CO$); 3.73 d, 1 H (CHCO); 3.90 – 5.18 m, 11 H (Fc, CH_2O, CHPh); 5.3 s, 1 H (=CH); 7.15 – 7.35 m, 5 H (Ph); 14.2 s, 1 H (OH). IR spectrum (NUJOL); 1 140, 1 257 (C–O); 1 603 (C=C); 1 657, 1 702, 1 712 (CO); 1 745 (CO–O); 3 455 (OH).

Addition of acetylacetone. Acetylacetone (5 mmol) and triethylamine (1.0 ml) were added to a solution of 2-benzylidene[3]ferrocenophane-1,3-dione (1.3 mmol) in anhydrous benzene (60 ml). The reaction mixture was heated under reflux for 7 h. After 1 h, a yellow compound precipitated. The precipitate was filtered off and the filtrate was evaporated. The residue was dissolved in benzene and the solvent was evaporated again (to remove the residual triethylamine). The precipitate and the crude material were combined and dissolved in hot benzene. After cooling, the benzene solution was chromatographed on Silpearl, eluent benzene–ethyl acetate. The unreacted 2-benzylidene[3]ferrocenophane-1,3-dione *I* (16%) was isolated from the first fraction. Compound *IIIa* (30%) was obtained from the second fraction, m.p. 170 – 180 °C. Small amount (about 20%) of yellow 4-acetyl-3-hydroxy-5-phenyl[7]ferrocenophane-2-ene-1,7-dione (*XII*) was isolated from the last fraction, m.p. 203 – 207 °C. For $C_{25}H_{23}FeO_4$ (442.3) calculated: 67.88% C, 5.01% H; found: 68.51% C, 4.99% H. ^{1}H NMR spectrum: 1.75 s, 3 H (CH_3); 2.60 d, ^3J(H,H) = 18.3, 1 H (CH_2); 3.01 d, ^3J(H,H) = 18.3, 1 H (CH_2); 3.2 s, 2 H ($COCH_2CO$); 3.76 d, ^3J(H,H) = 9.7, 1 H (CHCO); 4.09 m, 1 H (Fc); 4.12 m, 1 H (Fc); 4.46 m, 1 H (Fc); 4.51 m, 3 H (Fc); 4.62 d, ^3J(H,H) = 9.7, 1 H (CHPh); 4.71 m, 1 H (Fc); 4.75 m, 1 H (Fc); 5.16 s, 1 H (=CH); 7.1 – 7.4 m, 5 H (Ph); 16.21 s, 1 H (OH). IR spectrum (NUJOL): 1 600 (C=C); 1 657, 1 695, 1 700, 1 708 (CO); 3 364 (OH).

Reaction of Ethyl 3-Oxo-2-[2-(1,3-dioxo[3]ferrocenophanyl)phenylmethyl]-butanoate (*IIa*) with NH_3

Anhydrous ammonia was bubbled through a solution of *IIa* (0.6 mmol) in anhydrous benzene (50 ml) for 10 min. The compound *XIII* was immediately detected by TLC, but the rate of the reaction was slow and it was accelerated remarkably after addition of a small amount of silica. The crude product was filtered off, washed with benzene and crystallized. The dihydropyridine derivative *XIII* (77%) was isolated by crystallization, m.p. 249 – 251 °C. For $C_{26}H_{23}FeNO_3$ (453.3) calculated: 68.88% C, 5.11% H, 3.09% N, 12.32% Fe; found: 68.97% C, 5.11% H, 2.87% N, 12.05% Fe. ^{1}H NMR spectrum: 1.26 t, 3 H (CH_3); 2.39 s, 3 H (CH_3C=); 4.13 q, 2 H (CH_2); 4.26, 4.28, 4.29, 4.35, 4.38, 4.41, 4.45 and 4.50 m, 8 H (Fc); 5.21 s, 1 H (CHPh); 6.11 bs, 1 H (NH); 7.15 – 7.45 m, 5 H (Ph). The signal at δ 6.11 disappeared on addition of D_2O. ^{13}C NMR spectrum: 14.29 (CH_3); 19.36 (CH_3C=); 39.99 (CHPh); 59.95 (CH_2); 71.45, 71.60, 71.65, 71.77, 72.08, 72.22, 74.17, 77.22 and 85.89 (Fc); 104.80 (=C–COO); 118.86 (=CCO); 126.26, 127.71, 128.10 and 143.31 (Ph); 144.43 (=CCH_3); 147.08 (=CFc); 167.33 (COO); 193.11 (CO). IR spectrum ($CHCl_3$): 1 100, 1 210 (C–O); 1 636, 1 648 (C=C); 1 692 (C=O); 1 700 (CO–O); 3 428 (NH).

Reaction of 3-(2-(1,3-Dioxo[3]ferrocenophanyl)phenylmethyl)-2,4-pentanedione (*IIIa*) with Ammonia

The reaction was carried out under the same conditions as above. Compound *XIV* (80%), obtained by chromatography on Silpearl, did not melt up to 360 °C (benzene). For $C_{25}H_{21}FeNO_2$ (423.3) calculated: 70.93% C, 5.00% H, 3.30% N; found: 69.94% C, 5.43% H, 2.73% N. ^{1}H NMR spectrum: 2.22 s, 3 H (CH_3); 2.42 s, 3 H (CH_3CO); 4.24 – 4.5 m, 8 H (Fc); 5.23 s, 1 H (CHPh); 6.1 bs, 1 H (NH); 7.17 – 7.42 m, 5 H (Ph). IR spectrum (Nujol): 1 570, 1 595 (C=C); 1 665 (CO); 1 725; 3 290 (NH).

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Translation revised by M. Tichý.