Journal of Organometallic Chemistry, 132 (1977) 419—427
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SYNTHESIS AND REACTIVITY OF [3]FERROCENOPHANE-1,3-DIONE

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(Received December 22nd, 1976)

Summary

Synthesis of [3]ferrocenophane-1,3-dione, and its 2-substituted derivatives by internal Claisen condensation of methyl 1'-acylferrocenecarboxylates is described Reactions of the parent compound with alkyl halides and with benzaldehyde under basic conditions have been investigated

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Introduction

Considerable effort has been devoted to study of the reactions of cyclic 1,3-diketones such as 1,3-indandione [1], 2,3-dihydrophenalene-1,3-dione [2], and 5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene[3] Similar ferrocene derivatives e g [3]ferrocenophane-1,3-dione could not be studied because no synthesis had been described, though [3]ferrocenophane-1,3-dione is said to be a by-product of the oxidation of [3]ferrocenophane [4]

The aim of this work was to prepare [3]ferrocenophane-1,3-dione, to find methods of the synthesis of its 2-substituted derivatives, and compare its reactions with those of other cyclic 1,3-diketones

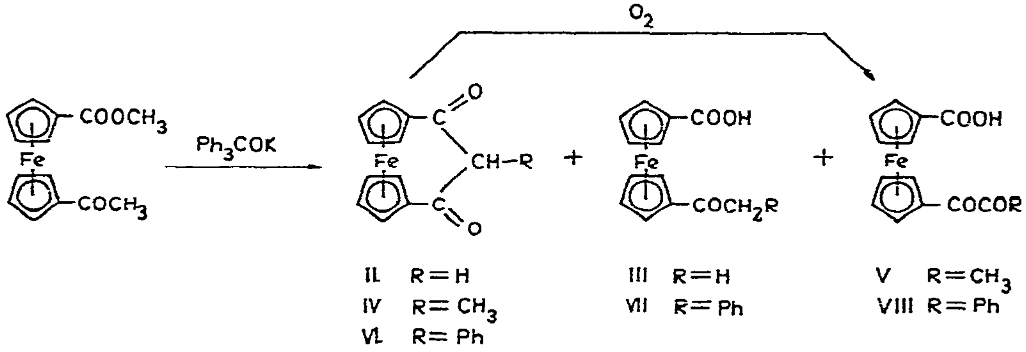
Results and discussion

Two compounds were chosen as starting materials for the synthesis of [3]ferrocenophane-1,3-dione (II), viz dimethyl 1,1'-ferrocenedicarboxylate and methyl 1'-acetylferrocenecarboxylate. Attempts to prepare II by Claisen condensation of dimethyl 1,1'-ferrocenedicarboxylate with methyl acetate, under conditions which were used for the preparation of 5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]-cycloheptene [5], were unsuccessful

We have used several methods for the cyclization of methyl 1'-acetylferrocenecarboxylate Attempts to prepare II by t-C_4H_9OK catalysis in benzene, both at room temperature or at reflux temperature, were unsuccessful, and only 1'-acetylferrocenecarboxylic acid was isolated. The same result was obtained with Ph_3COK catalysis in xylene at room temperature The same catalyst in refluxing xylene gave a high yield of the desired product (up to 78%) Šraga [6] has used the same method for the synthesis of 1,3-cyclopentanedione in high yield.

From these results, it can be concluded that a high activation energy is involved in the cyclization This conclusion was confirmed by the observation that catalysis with t-C_4H_9OK in boiling xylene also gave the desired product II in 50% yield Potassium t-butoxide was found to be a less effective catalyst than Ph_3COK for cyclization of methyl 1'-acetylferrocenecarboxylate (Scheme 1)

SCHEME 1



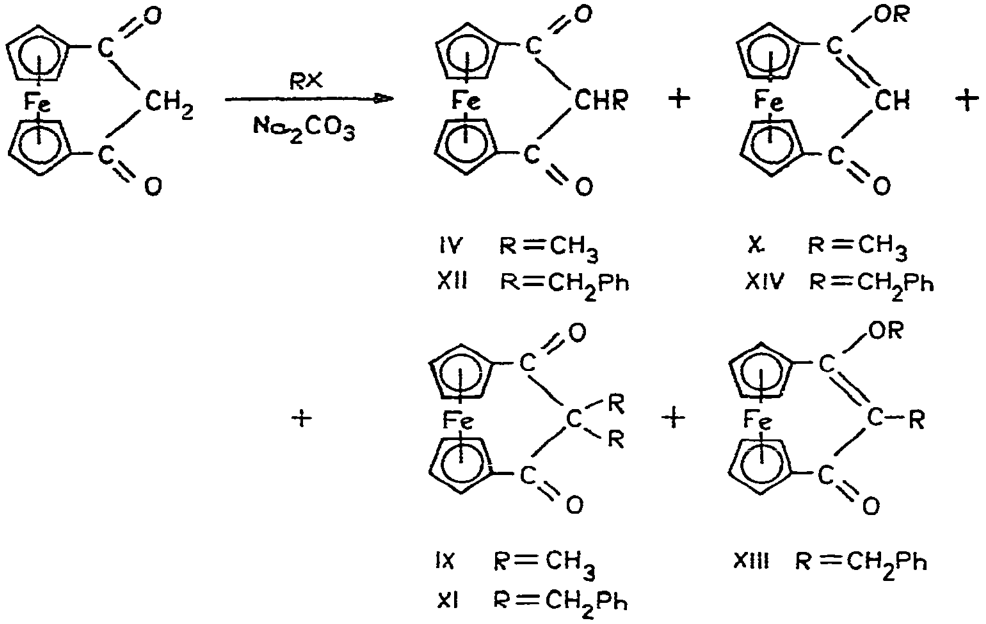
2-Substituted [3]ferrocenophane-1,3-diones can by synthesised by the same method, as represented in Scheme 1 The preparation of necessary intermediates e g methyl 1'-acylferrocenecarboxylates caused no problems. Cyclization of these intermediates went smoothly, but there are sometimes considerable losses during the isolations of the cyclizates The solution of 2-methyl[3]ferrocenophane-1,3-dione was found to be very sensitive to the air, it is oxidised by air, with opening of the bridge, to the 1'-pyruvoylferrocenecarboxylic acid The oxidation was monitored by TLC The oxidation product VIII formed from 2-phenyl[3]ferrocenophane-1,3-dione was also isolated

Previously, a high sensitivity towards air was observed only for ferrocene derivatives containing a methylene group between the ferrocene moiety and an electron-atracting group This was shown by formation of pyruvoylferrocene during the synthesis of ferrocenylacetone [7]

Because the ferrocenecarboxylic acid was readily prepared by acid cleavage of *o*-chlorobenzoylferrocene [8], we decided to cyclize 1'-acetyl-1-(*o*-chlorobenzoyl)ferrocene under the same conditions, but only starting material, heavily contaminated with triphenylmethanol, was recovered.

The other method for synthesis of 2-alkyl[3]ferrocenophane-1,3-diones is alkylation of the carbanion generated from the parent compound II. This method, represented in Scheme 2, does not give simple results because all possible mono- and di-alkylation products are formed The main product, in acetone or DMF, is always the result of *O*-alkylation, in contrast to the results observed on alkylation of 2-phenyl-1,3-indandione [1], 2-phenyl-2,3-dihydrophenalene-1,3-

SCHEME 2



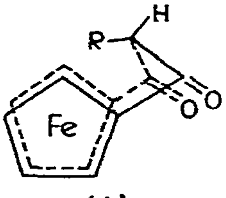
IV $R=CH_3$
XII $R=CH_2Ph$

X $R=CH_3$
XIV $R=CH_2Ph$

IX $R=CH_3$
XI $R=CH_2Ph$

XIII $R=CH_2Ph$

dione [2] or 6-phenyl-5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene [3] This can be attributed to the different type of solvation [9] if one assumes a U-shape conformation for the carbanione formed from II The inspection of a Dreiding model of II showed that such conformation is impossible for II, but revealed that α-hydrogens of the Cp ring can cause steric hindrance for the attack of alkyl halide on the CH_2 group of the bridge (see A) No such hindrance is involved for attack on the oxygen of the carbonyl group

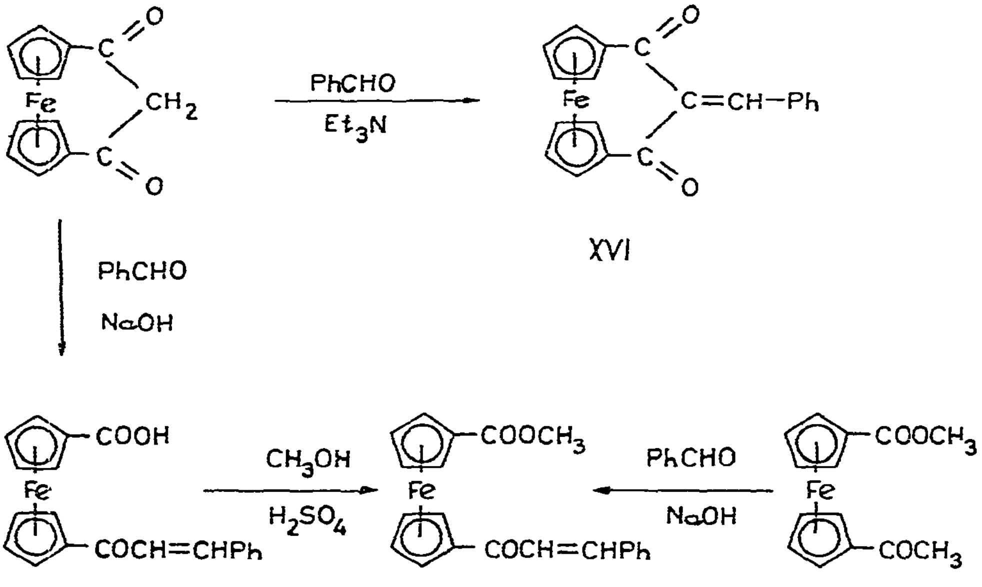


(A)

Some evidence for such steric hindrance by the α-hydrogen atoms of the Cp ring were found in the PMR spectra of 2-alkyl(aryl)[3]ferrocenophane-1,3-diones (compounds IV, VI and XII). Because both Cp rings bear the same substituent, viz. the carbonyl group, the protons of the cyclopentadienyl group should absorb as two four-proton triplets, as is with the parent compound In fact there appears a two proton signal at the lower field (near δ 4 92 ppm), and a 7 proton multiplet in the region δ 4 25—4 65 ppm This can be explained if we assume that two protons of four α-hydrogens are shielded by the alkyl group, and therefore their resonance is at higher field, along with that for H_β and the CH of the bridge

Condensation of [3]ferrocenophane-1,3-dione with benzaldehyde with NaOH catalysis gave rise to the 1′-cinnamoylferrocenecarboxylic acid (XV). The PMR spectrum of XV is consistent with the proposed structure, but the compound has a broad m.p., and therefore we decided to confirm the structure by synthetic means also The acid XV was transformed into its methyl ester XVII, the properties of which were identical with the product of condensation of methyl 1′-acetylferrocenecarboxylate with benzaldehyde

SCHEME 3



XVI

XV

XVII

With triethylamine catalysis the condensation of II with benzaldehyde proceeded easily without opening of the bridge, and XVI was isolated in high yield In this respect there are great differences in the reactivity of II and the cyclic β-diketones mentioned in the introduction 1,3-Indandione forms auto-condensation products under NaOH catalysis [10], and 5,7-dioxo-6,7-dihydro-5*H*-dibenzo-[*a*,*c*]cycloheptene with benzaldehyde gives 1/1 as well as 1/2 condensation products under triethylamine catalysis [11]

It is noteworthy that in the case of 3-alkyloxy[3]ferrocenophane-2-ene-1-ones (X, XIV), as in the case of 2-benzal[3]ferrocenophane-1,3-dione (XVI) we have ferrocenophanes which contain all sp^2 hybridised carbon atoms in the birdge. There must be a considerable ring-tilting in these derivatives if we assume the coplanarity of the cyclopentadienyl rings and carbonyl groups On the other hand, the ring-tilting would be minimised if the carbonyl groups were out of the plane of the Cp rings.

Comparison of the UV spectra of II and IV with X and XVI reveals that there mus be some conjugation between Cp rings and the C=C bond in X or the Cp ring and the =CH—Ph group in XVI because they have λ_{max} at 435 and 462 nm, but no discrete maxima were observed in the visible region of II and IV The conjugation in XVI is less pronounced than in the non-bridged compound XV (λ_{max} 485 nm)

Elucidation of this problem may require X-ray diffraction studies of the crystals

Experimental

PMR spectra were recorded at 25°C on a Tesla BS 487 instrument at 80 MHz The spectra were recorded in $CDCl_3$ (99 5% of D-isotope) or $(CD_3)_2SO$ solutions with tetramethylsilane or HMDSO as internal standards All chemical shifts are relative to TMS, and are accurate to ±0 01 ppm UV spectra (in MeOH) were recorded on a Perkin—Elmer UV-Vis 450 spectrometer Chromatography was carried out on SiO_2 (Kavalier, Votice) or Al_2O_3 (Brockman II, Reanal Budapest), and the products are given in the sequence of elution Melting points were determined on a Kofler apparatus and are uncorrected All synthesis were carried out under purified N_2

Methyl 1'-phenylacetylferrocenecarboxylate (I)

To a stirred solution of 2 5 g (0 01 mol) of methyl ferrocenecarboxylate in 50 ml of carbon tetrachloride, 3 1 g (0 02 mol) of anhydrous $AlCl_3$ was added with ice-cooling Phenylacetyl chloride, (5 g, 0 035 mol) in 50 ml of carbon tetrachloride was then added dropwise to the stirred and cooled mixture, which was then stirred at room temperature for one hour and poured into ice-water The organic material was extracted with CCl_4 Extracts were carefully washed with water and with 10% Na_2CO_3 solution to hydrolyse the unreacted phenylacetyl chloride The CCl_4 solution was dried over anhydrous Na_2SO_4 The residue left after evaporation of the solvent was chromatographed on Al_2O_3 with 9/1 benzene/ethyl acetate to give 2 5 g (70%) of I, m p. 123—125°C (benzene). [Found. C, 66 70, H, 5 23, Fe, 15 39, mol wt 362 2 $C_{20}H_{18}FeO_3$ calcd C, 66 32; H, 5 01, Fe, 15 42%] PMR[$(CD_3)_2SO$] (ppm) $\delta(CH_3)$ 3 72 (s, 3H), $\delta(CH_2)$ 4 03 (s, 2H), $\delta(H_\beta)$ 4 48 (t, 2H), $\delta(H_\beta')$ 4 60 (t, 2H); $\delta(H_\alpha)$ 4 77 (t, 2H), $\delta(H_\alpha')$ 4.88 (t, 2H), $\delta(C_6H_5)$ 7 29 (app s, 5H)

Cyclization of methyl 1'-acetylferrocenecarboxylate

A hot solution of 16 g (0 06 mol) of triphenylmethanol in 150 ml of xylene was added to the stirred suspension of 2 g (0.05 g-atom) of potassium in 120 ml of refluxing xylene The mixture was stirred at the reflux temperature until all the Ph_3COK dissolved The stirring was then stopped, and a solution of 5 6 g (0 02 mol) of methyl 1'-acetylferrocenecarboxylate [12] in 200 ml of xylene was added very slowly, at a rate of one drop every 3—4 sec, to the refluxing mixture. All the methyl 1'-acetylferrocenecarboxylate was added during 3 h

The mixture was refluxed, without stirring, for an additional 2 h, and then cooled very slowly to 0°C Ice-water (250 ml) was added to the stirred and cooled mixture, the aqueous layer was separated, and triphenylmethanol was filtered off from the xylene solution The organic layer was washed with water, and the aqueous layers were combined, filtered and acidified to pH 2—3 with dilute HCl Organic material was extracted, partially as a solid, into dichloromethane, the extract was dried (Na_2SO_4) and the solvent was evaporated The residue was chromatographed on SiO_2 with 3/1 benzene/ethyl acetate as the eluent. Small amounts of unidentified material was isolated from the first, yellow band. From the second orange-red band was isolated 3 9 g (78%) of [3]ferrocenophane-1,3-dione (II), m p 163—165°C (benzene/petroleum ether). Found· C, 61.65, H, 3 96, Fe, 21 84, mol. wt 254 07 $C_{13}H_{10}FeO_2$ calcd · C, 61.45; H, 3 96; Fe, 21 98%] PMR [$CDCl_3$] (ppm) $\delta(CH_2)$ 3 96 (s, 2H), $\delta(H_\beta)$ 4.56 (t, 4H), $\delta(H_\alpha)$ 4.73 (t, 4H); UV (nm(ϵ)) 221 ($1\ 34 \times 10^4$), 257 (sh) (9.6×10^3), 315 ($1\ 1 \times 10^3$), 345 ($1\ 12 \times 10^3$) MS *m/e* $[C_{13}H_{10}FeO_2]^+$ 253 996 → *m/e* $[C_{11}H_{10}Fe]^+$ 198.011 Other. the most intensive fragments *m/e* $[C_7H_6FeO]^+$ 161 982 and *m/e* $[C_6H_6Fe]^+$ 133 982

From the third, red band was isolated 0.4 g (7%) of 1′-acetylferrocenecarboxylic acid (III) m p 155—157°C (benzene), in accord with ref. [13]. PMR [$CDCl_3$] (ppm) $\delta(CH_3)$ 2 44 (s, 3H), $\delta(H_\beta)$ 4 48 (t, 2H), $\delta(H_\beta)$ 4 58 (t, 2H); $\delta(H_{\alpha,\alpha})$ 4 86 (t, 4H), $\delta(COOH)$ 10 45 (broad s, 1H)

Cyclization of methyl 1′-propionylferrocenecarboxylate

The reaction was carried out as described above with 1 5 g (5 mmol) methyl 1′-propionylferrocenecarboxylate [12], 0 5 g (12 5 mg-atom) K, and 3 9 g (15 mmol) triphenylmethanol Chromatography afforded 0 8 g (60%) of 2-methyl[3]ferrocenophane-1,3-dione (IV) m p 138—143°C (benzene/petroleum ether), from the first, orange-yellow band [Found C, 62 21, H, 4 40, Fe, 21 02, mol wt. 268 1 $C_{14}H_{12}FeO_2$ calcd C, 62 72, H, 4 51, Fe, 20 83%] PMR [$CDCl_3$] (ppm) $\delta(CH_3)$ 1 39 (d, 3H), $\delta(CH)$ 4 39 (q, 1H), $\delta(H_\alpha\ H_\beta)$ 4 48 (m, 6H), $\delta(H_\alpha)$ 4 93 (p, 2H), UV, (nm (ϵ)) 220 ($1\ 09 \times 10^4$), 257 (sh) ($8\ 4 \times 10^3$), 350 ($1\ 14 \times 10^3$)

From the second, violet band was isolated 0 05 g (3 7%) of 1′-pyruvoylferrocenecarboxylic acid (V) m p 114—116°C (benzene/n-heptane) [Found C, 55 93, H, 4 08; Fe, 18 74, mol wt 300.1. $C_{14}H_{12}FeO_4$ calcd C, 56 03, H, 4 03, Fe, 18 33%] PMR [$CDCl_3$] (ppm) $\delta(CH_3)$ 2.51 (s, 3H), $\delta(H_\beta)$ 4 50 (t, 2H); $\delta(H_\beta)$ 4.74 (t, 2H), $\delta(H_\alpha)$ 4 89 (t, 2H), $\delta(H_\alpha)$ 5 15 (t, 2H), $\delta(COOH)$ 9 25 (broad s, 1H)

Note All the solutions have to be worked-up very quickly, because IV is very easily oxidized to V by the air, as indicated by TLC monitoring

Cyclization of methyl 1′-phenylacetylferrocenecarboxylate

The reaction was carried out as described above on 0 45 g (1 25 mmol) of I, 0 15 g (3.8 mg-atom) of K, and 1 g (4 mmol) of triphenylmethanol After addition of water, 0 3 g of solid was collected, which was practically insoluble in CH_2Cl_2, Et_2O or benzene. Crystallization from methanol afforded 80 mg (19 5%) of straw-yellow 2-phenyl[3]ferrocenophane-1,3-dione (VI) m p 360°C [Found C, 69 05, H, 4 32, Fe, 16 87; mol wt 330 16 $C_{19}H_{14}FeO_2$ calcd · C, 69 12, H, 4 27, Fe, 16 91%] PMR [$(CD_3)_2SO$] (ppm). $\delta(C_5H_4)$ 4 35—4 80 (m, 8H). $\delta(CH)$ 5 55 (s, 1H), $\delta(C_6H_5)$ 7 15—7 75 (m, 5H)

The mother liquor from the cyclization was evaporated, and the residue was crystallized from benzene Red crystals (200 mg, 44 2%) of 1′-phenylacetyl ferrocenecarboxylic acid (VII) m p 194—199°C were isolated. [Found C, 65.74, H, 4.82, Fe, 16.03, mol. wt. 348 18, $C_{19}H_{16}FeO_3$ calcd : C, 65 54, H, 4 63, Fe, 16.04%.] PMR [$(CD_3)_2SO$] (ppm). $\delta(CH_2)$ 4 05 (s, 2H), $\delta(H_\beta)$ 4 43 (t, 2H), $\delta(H_\beta)$ 4.59 (t, 2H); $\delta(H_\alpha)$ 4 70 (t, 2H), $\delta(H_\alpha)$ 4 84 (t, 2H), $\delta(C_6H_5)$ 7 29 (app s, 5H). Chromatography of the benzene mother liquor from this crystallization afforded a small amount of VII, and 0 05 g (11%) of 1'-phenylglyoxyloylferrocenecarboxylic acid (VIII) m p 170—180°C (benzene) [Found· C, 63 03, H, 4 01, Fe, 15 71; mol wt 362 16 $C_{19}H_{14}FeO_4$ calcd C, 62 84, H, 3 90, Fe, 15 42%] PMR [$CDCl_3$] (ppm) $\delta(H_\beta)$ 4 55 (t, 2H), $\delta(H_\beta)$ 4 71 (t, 2H), $\delta(H_{\alpha\,\alpha})$ 4.94 (m, 4H), $\delta(C_6H_5)$ 7.2—8.17 (m, 5H), $\delta(COOH)$ 8.6 (broad s, 1H)

Methylation of [3]ferrocenophane-1,3-dione

To a stirred solution of 0.6 g (2 5 mmol) or II in 65 ml anhydrous acetone was added 1 g (7 5 mmol) of K_2CO_3. Methyl iodide (0 5 ml, 7 mmol) was added dropwise The mixture was filtered, and the solid wasned twice with benzene The acetone and benzene solutions were combined, and the solvent was evaporated under reduced pressure. The residue was chromatographed on SiO_2, benzene containing 5—10% of ethyl acetate being used as the eluent Chromatography gave 40 mg (6%) of 2,2-dimethyl[3]ferrocenophane-1,3-dione (IX) m p 179—181°C (benzene/petroleum ether) [Found C, 64 42, H, 5 35, Fe, 19 48, mol wt 282 13. $C_{15}H_{14}FeO_2$ calcd C, 63 86, H, 5 00, Fe, 19 77%] PMR [$CDCl_3$] (ppm) $\delta(CH_3)$ 1 53 (s, 6H), $\delta(H_\beta)$ 4 55 (t, 4H), $\delta(H_\alpha)$ 4 67 (t, 4H) From the second band 120 mg (20%) of IV, and from the third band 350 mg (55 5%) of 3-methoxy[3]ferrocenophane-2-one-1-one (X) m p. 108—109°C (benzene/petroleum ether) were isolated [Found C, 62.76, H, 4 50, Fe, 20.64, mol wt 268 10 $C_{14}H_{12}FeO_2$ calcd C, 62 72, H, 4 51, Fe, 20 83%] PMR [$CDCl_3$] (ppm) $\delta(OCH_3)$ 3.73 (s, 3H), $\delta(H_{\beta\,\beta})$ 4 29 (m, 4H), $\delta(H_{\alpha\,\alpha})$ 4 37—4 55 (m, 4H). $\delta(=CH)$ 5 80 (s, 1H), UV (nm (ϵ)) 214 (1 11 × 10^4), 239 (sh) (8 55 × 10^3), 366 (7 2 × 10^2), 435 (5.4 × 10^2) From the last band 30 mg (4%) of V was isolated.

Benzylation of [3]ferrocenophane-1,3-dione in acetone

The reaction was carried out as described above on 0 3 g (1 2 mmol) of II, 0 22 ml (1 8 mmol) of benzyl bromide, 0 5 g (3 5 mmol) of K_2CO_3, and 35 ml of acetone Chromatography afforded

(a) 5 mg (1%) of 2,2-dibenzyl[3]ferrocenophane-1,3-dione (XI) m p 195—200°C [Found C, 74.07; H, 5 91, Fe. 11 51, mol wt 434 32 $C_{27}H_{22}FeO_2$ calcd C, 74 67; H, 5 11, Fe, 12 86%] PMR [$CDCl_3$] (ppm) $\delta(CH_2)$ 3 36 (s, 4H), $\delta(C_5H_4)$ 4 25—4 42 (m, 8H), $\delta(C_6H_5)$ 7 23 (s, 1H).

(b) 20 mg (5%) of 2-benzyl[3]ferrocenophane-1,3-dione (XII) m p 191—193°C (benzene/petroleum ether) [Found C, 70 32, H, 5 13; Fe, 16 02, mol wt 344 20. $C_{20}H_{16}FeO_2$ calcd C, 69.79, H, 4 69, Fe, 16 23%] PMR [$CDCl_3$] (ppm) $\delta(CH_2)$ 3 33 (d, 2H), $\delta(H_{\beta,\alpha}\ CH)$ 4 50 (m, 7H), $\delta(H_\alpha)$ 4 85 (m, 2H), $\delta(C_6H_5)$ 7 24 (m, 5H)

(c) 40 mg (8%) of 3-benzyloxy-2-benzyl[3]ferrocenophane-2-ene-1-one (XIII) m p 132—137°C (diethyl ether) [Found C, 74 15, H, 5 08, Fe, 12 98, mol wt 434 32 $C_{27}H_{22}FeO_2$ calcd C, 74 67, H, 5 11, Fe, 12 86%] PMR [$CDCl_3$] (ppm) $\delta(CH_2)$ 3 85 (s, 2H), $\delta(C_5H_4)$ 4 17—4 51 (m, 8H), $\delta(OCH_2)$ 4 90 (s, 2H), $\delta(C_6H_5)$ 7 0—7.4 (m, 10H)

(d) 240 mg (60%) of 3-benzyloxy[3]ferrocenophane-2-ene-1-one (XIV) m.p. 113—114°C (benzene/n-hexane) [Found C, 69.60; H, 4.67, Fe, 16.65; mol. wt. 344.20. $C_{20}H_{16}FeO_2$ calcd. C, 69.78, H, 4.69, Fe, 16.23%.] PMR [$CDCl_3$] (ppm): $\delta(H_\beta)$ 4.29 (t, 2H), $\delta(H_\beta)$ 4.31 (t, 2H). $\delta(H_\alpha)$ 4.47 (t, 2H); $\delta(H_\alpha)$ 4.51 (t, 2H), $\delta(OCH_2)$ 4.96 (s, 2H), $\delta(=CH)$ 5.92 (s, 1H), $\delta(C_6H_5)$ 7.33 (app. s, 5H)

Benzylation of [3]ferrocenophane-1,3-dione in DMF

The reaction was carried out as described above, but with DMF as the solvent. Chromatography gave 20 mg (4%) of XI, 80 mg (16%) of XIII, and 280 mg (65%) of XIV.

Condensation of 3 ferrocenophane-1,3-dione with benzaldehyde

(A) Catalysis with NaOH Benzaldehyde (0.2 ml, 3 mmol) and 5 ml of 10% NaOH were added to a stirred solution of 0.5 g (2 mmol) of II in 20 ml of ethanol warmed to 50°C. After 5 hours stirring at 50—65°C the mixture was cooled to room temperature then was added to a large amount of water. The aqueous layer was washed with chloroform, only a small amount of organic material was extracted, as indicated by the colour and TLC. The aqueous layer was acidified with dilute HCl, and again extracted with chloroform. The chloroform solution was dried (Na_2SO_4) and the solvent was evaporated. Chromatography of the residue on an SiO_2 column with benzene containing 10—25% of ethyl acetate as the eluent gave traces of unidentified material, traces of II (TLC), then 0.35 g (50%) of 1′-cinnamoylferrocenecarboxylic acid (XV) m.p. 165—170°C (benzene) [Found C, 66.65, H, 4.32, Fe, 15.45, mol. wt. 360.20. $C_{20}H_{16}FeO_3$ calcd.: C, 66.68, H, 4.47, Fe, 15.50%.] PMR [$CDCl_3$] (ppm). $\delta(H_\beta)$ 4.48 (t, 2H), $\delta(H_\beta)$ 4.63 (t, 2H), $\delta(H_\alpha)$ 4.86 (t, 2H), $\delta(H_{\alpha'})$ 4.95 (t, 2H); $\delta(CH=CH)$ 7.15 (1H) and 7.77 (1H) (AB quartet J_{AB} 15.5 Hz), $\delta(C_6H_5, OH)$ 7.2—7.67 (m, 6H). UV (nm (ϵ)) 220 (2.36×10^4), 258 (1.44×10^4), 307 (2.56×10^4), 485 (1.54×10^3). From the last band was isolated 0.15 g (28%) of III

(B) Triethylamine catalysis Triethylamine (1.5 ml) was added to a stirred refluxing solution of 0.5 g (2 mmol) of II, and 0.75 ml (7 mmol) of benzaldehyde in 40 ml of anhydrous benzene. The mixture was stirred under reflux for 7 h. The residue left after evaporation of the solvent was chromatographed on SiO_2 with benzene containing 10—15% ethyl acetate as the eluent. Traces of XV and III were detected by TLC, but were not isolated. From the main, deep red band was isolated 0.45 g (66.2%) of 2-benzal[3]ferrocenophane-1,3-dione (XVI) m.p. 169—171°C (benzene/petroleum ether). [Found: C, 69.56, H, 4.18; Fe, 16.23; mol. wt. 343.19. $C_{20}H_{14}FeO_2$ (calcd. C, 69.99, H, 4.40, Fe, 16.27%.] PMR [$CDCl_3$] (ppm). $\delta(H_\beta)$ 4.54 (t, 4H), $\delta(H_\alpha)$ 4.73 (t, 4H), $\delta(C_6H_5)$ 7.2—7.75 (m, 5H); $\delta(=CH)$ 7.88 (s, 1H). UV (nm (ϵ)) 210 (1.78×10^4), 232 (1.08×10^5), 315 (1.74×10^4), 462 (8.4×10^2)

Condensation of 1′-acetylferrocenecarboxylic acid with benzaldehyde

To a stirred solution of 0.55 g (2 mmol) of III and 0.5 ml (5 mmol) of benzaldehyde in 40 ml of methanol was added 5 ml of 10% NaOH. The mixture was stirred at room temperature for 5 hours and then poured into water. The aqueous solution was acidified and the organic material was extracted into dichloromethane. The dichloromethane solution was dried (Na_2SO_4) and the solvent evaporated The residue was chromatographed on SiO_2 with 3/1 benzene/ethyl acetate as the eluent Deep red crystals of XV (0 45 g, 60%) were isolated and 0 1 g (18%) of the starting material was recovered

Esterification of 1'-cinnamoylferrocenecarboxylic acid

Three drops of concentrated H_2SO_4 were added to a solution of 0 25 g (0.7 mmol) of XV in 50 ml of methanol, and the mixture was refluxed for 5 hours The mixture was added to water and the organic material extracted into dichloromethane The residue left after evaporation of the solvent was chromatographed on SiO_2 to give 0 25 g (95%) of deep-red crystals of methyl 1'-cinnamoylferrocenecarboxylate (XVII) This compound exhibits allotropy, it has m p 's of 65—70°C and 125—130°C (benzene/petroleum ether) [Found C, 67 35, H, 4 69, Fe, 14 15, mol wt 374 22 $C_{21}H_{18}FeO_3$ calcd C, 67 40, H, 4 84, Fe, 14 90%] PMR [$CDCl_3$] (ppm) $\delta(CH_3)$ 3 76 (s, 3H), $\delta(H_\beta)$ 4 40 (t, 2H), $\delta(H_{\beta'})$ 4 56 (t, 2H), $\delta(H_\alpha)$ 4.82 (t, 2H), $\delta(H_{\alpha'})$ 4 91 (t, 2H), δ(CH=CH) 7 10 (1H) and 7 78 (1H) (AB quartet J_{AB} 15.6 Hz), $\delta(C_6H_5)$ 7 22—7 62 (m, 5H)

Condensation of methyl 1'-acetylferrocenecarboxylate with benzaldehyde

The mixture of 0 55 g (2 mmol) of methyl 1'-acetylferrocenecarboxylate, 0 75 ml (7 mmol) of benzaldehyde, and 5 ml of 10% NaOH in 40 ml of methanol was stirred at room temperature for 5 hours, After the usual work-up, chromatography gave many bands, but only two compounds were isolated, viz red crystals of XVII (0 18 g, 25%), and 0 3 g (42%) of XV This time the m p of XV was 167—168°C

Acknowledgements

Our thanks are due to Dr E Greiplová (Comenius University) for elemental analyses, and Prof P L Pauson (University of Strathclyde) for mass spectra

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