

BRIDGED FERROCENES—I

THE SYNTHESIS AND CONFORMATION OF [5]FERROCENOPHANES

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(Received in the UK 18 October 1967; accepted for publication 30 October 1967)

Abstract—The synthesis of a wide range of [5]ferrocenophanes has been achieved. The structure and conformation of these compounds are discussed in the light of their spectral properties and compared with the results previously reported for the [3] and [4] series.

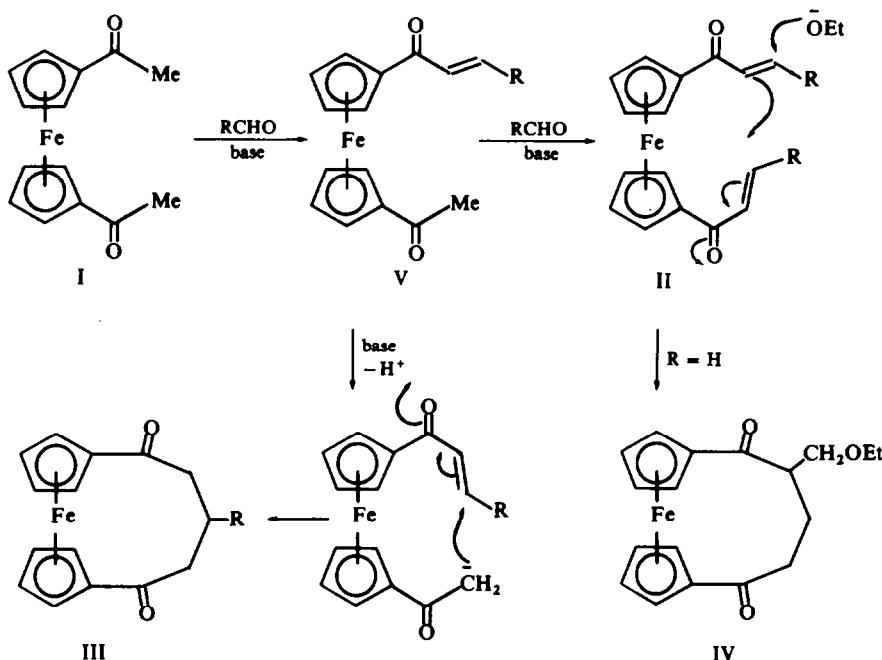
INTRODUCTION

SINCE the discovery of ferrocene was reported¹ in 1951, the synthesis of derivatives in which the cyclopentadienyl rings are linked by a carbon chain has attracted considerable interest.² This research activity has led to the preparation of a large number of heteroannularly bridged ferrocenes, designated³ [m]ferrocenophanes, with bridge lengths varying from 2 to 10 carbon atoms. The readily accessible [3]ferrocenophanes have been thoroughly studied but comparatively little systematic work has been directed towards related systems of different bridge length. In this paper, various synthetic approaches to the [5]ferrocenophane class are described,⁴ and the molecular geometry of compounds of this type is discussed in terms of their spectral characteristics.

SYNTHETIC ROUTES

In 1960, Hauser *et al.* reported⁵ that the base-catalysed condensation of 1,1'-diacetylferrocene (I) with benzaldehyde afforded, in addition to the expected 1,1'-dicinnamoylferrocene (II; R = Ph), a second product for which several possible structures were suggested. On the basis of IR and UV spectral evidence, on the other hand, Furdik *et al.* reformulated⁶ this compound as 3-phenyl[5]ferrocenophane-1,5-dione (III; R = Ph) and showed that a range of products of related structure could be prepared using other aromatic^{6,7} as well as aliphatic aldehydes.⁸ We have reinvestigated this reaction and isolated a substance with properties identical to those previously reported.^{5,6} The spectral properties of this compound together with its chemical reactions (described later) conclusively establish the bridged structure (III; R = Ph) originally proposed⁶ by Furdik.

Since our interest was primarily concerned with the parent [5]ferrocenophane system, the condensation between I and formaldehyde in aqueous ethanolic sodium hydroxide solution was also reinvestigated. In addition to the bridged diketone (III; R = H) described⁸ by Furdik *et al.*, we isolated as the main product of this reaction a compound to which the 2-ethoxymethyl[5]ferrocenophane-1,5-dione structure (IV) is assigned. The same substance was also formed on treatment of 1,1'-diacryloylferrocene (II; R = H) with sodium ethoxide in ethanol and it is probable that its formation in the condensation reaction proceeds by a related route.



A more practical entry into the parent system was realized by the quantitative base-catalysed cyclization of either 1-acetyl-1'-(β -chloropropionyl)ferrocene or 1-acetyl-1'-acryloylferrocene (V; R = H) to the diketone (III; R = H). Since the cinamoyl analogues (V; R = Ph, etc.) undergo similar intramolecular cyclization,⁶ the mechanism of the condensation between equimolar proportions of 1,1'-diacetylferrocene (I) and aldehydes is established as a Claisen-Schmidt reaction followed by internal Michael addition to form the interannular bridge.* The aforementioned acryloyl derivatives (II and V; R = H), which are unstable, were prepared by Friedel-Crafts reaction between the Perrier complex¹⁰ of β -chloropropionyl chloride and ferrocene† and acetylferrocene respectively. Purification of the products from these reactions by chromatography on silica gives the corresponding β -chloropropionyl derivatives which can be dehydrochlorinated by chromatography on alumina.

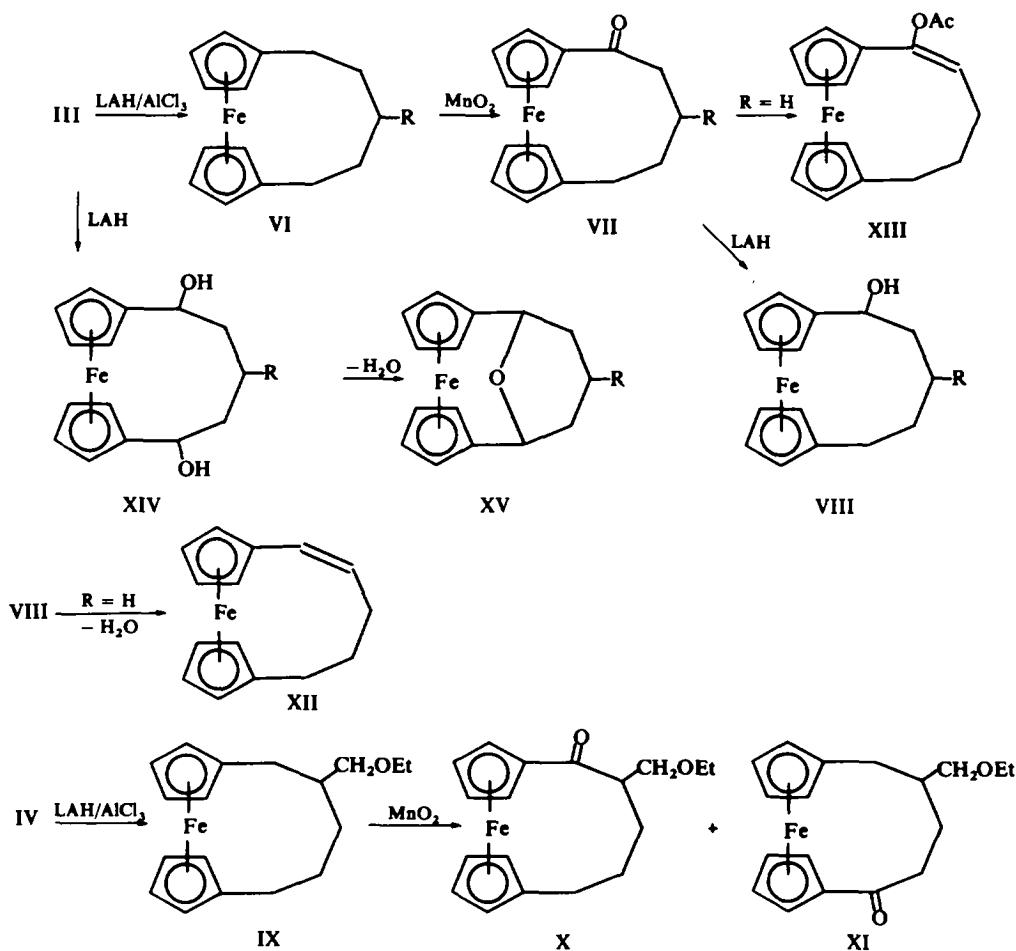
The diketone (III; R = H) was reduced by LAH-AlCl₃¹³ to [5]ferrocenophane (VI; R = H) whose properties were similar to those reported¹⁴ for this compound. The 3-phenyl derivative (VI; R = Ph) was similarly obtained from the diketone (III; R = Ph). This last reaction has apparently¹⁵ also been carried out by Schlögl. Manganese dioxide oxidation¹⁶ of the ferrocenophanes (VI; R = H and Ph) gave the monoketones (VII; R = H and Ph respectively) which in turn were reduced by lithium aluminium hydride to the alcohols (VIII; R = H and Ph respectively). By a

* During preparation of this manuscript, the intramolecular Michael cyclization of 1-acetyl-1'-acryloylferrocene to III (R = H) and the reduction of the latter compound to [5]ferrocenophane has been described.⁹

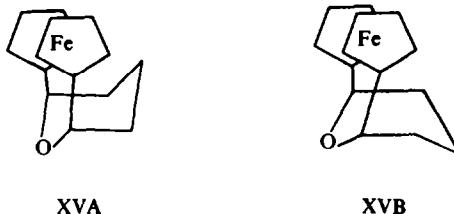
† The report¹¹ of the preparation of 1,1'-diacryloylferrocene (II; R = H) by this method was later retracted.¹²

similar sequence of reactions, the diketoether (IV) was converted to the ether (IX) and thence to the isomeric keto-ethers (X and XI). The isomers were separated chromatographically and their structures assigned from their PMR spectra (*vide infra*). In marked contrast to the difficulty in introducing unsaturation into the [3]ferrocenophane bridge,¹⁷ the alcohol (VIII; R = H) underwent ready phosphorus oxychloride-pyridine dehydration¹⁸ to [5]ferrocenophan-1-ene (XII) and the ketone (VII; R = H) could be smoothly converted to its enol-acetate (XIII).

The expected diol (XIV; R = H) was not obtained from hydride reduction of the diketone (III; R = H) but instead this reaction yielded the novel tetrahydropyran derivative (XV; R = H), presumably formed by facile intramolecular dehydration of the above diol. A compound of related structure (XV; R = Ph) was similarly obtained from the diketone (III; R = Ph) together with a product whose instability precluded satisfactory characterization, but whose IR spectrum was in accord with the diol (XIV; R = Ph). Acid alumina dehydration¹⁹ of this substance gave an ether different from that originally obtained. The m.ps and IR spectra of these ethers are similar but distinct and their PMR and mass spectra agree with their formulation as stereoisomeric forms of the tetrahydropyran derivative (XV; R = Ph).



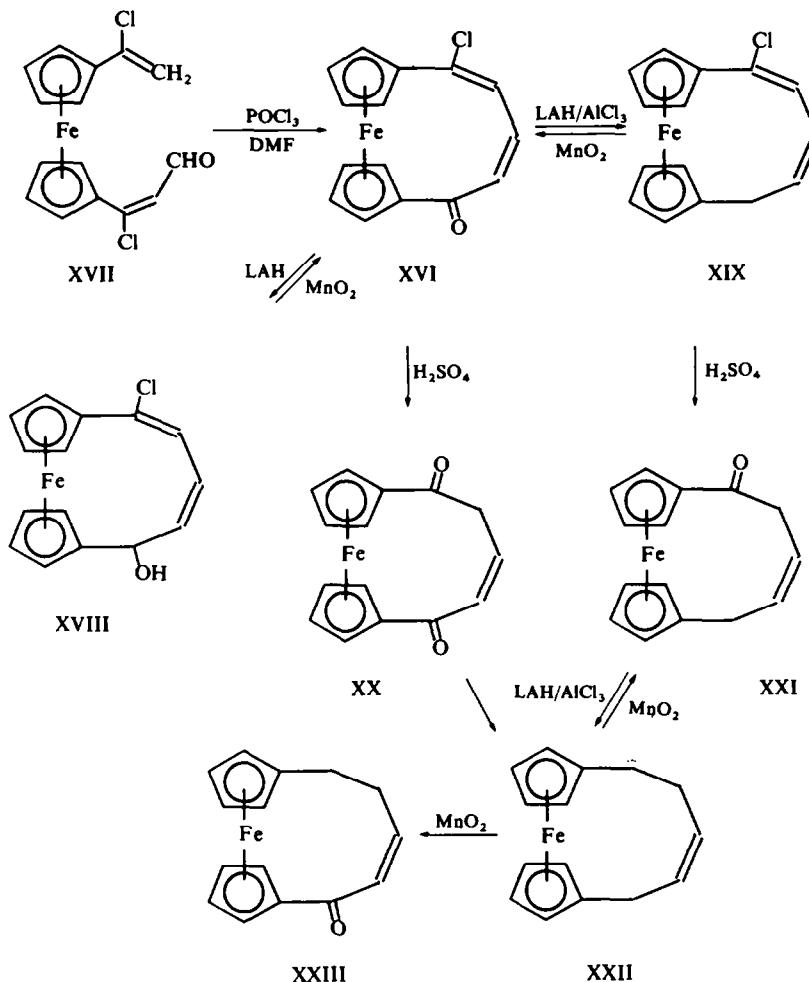
Of necessity, the cyclopentadienyl rings in the bridged ethers (XV) must be connected to the tetrahydropyran ring by axial bonds. The tetrahydropyran ring can presumably adopt a "chair" (XVA) or a "boat" conformation (XVB) but interconversion of these limiting structures by a ring-flip process would be energetically much more expensive than in the case of tetrahydropyran itself due to the constraint introduced by the bridging ferrocenylene residue. Four idealized structures can thus be considered for the two isomers (XV; R = Ph) with the phenyl substituent attached to the tetrahydropyran "chair" (XVA) or "boat" (XVB) in an axial or equatorial position. No decision between these possibilities has been reached although the axial phenyl-“chair” structure is considered unlikely due to unfavourable steric interaction between the phenyl and ferrocenylene residues.



Recently the 1-chloro[5]ferrocenophane-1,3-dien-5-one structure (XVI) has been tentatively assigned²⁰ to a product obtained from the unsaturated aldehyde (XVII) and phosphorus oxychloride in dimethylformamide.* We have used this compound to prepare several derivatives containing unsaturation in the bridge and the reactions described below fully substantiate the dienone structure (XVI) suggested²⁰ by Rosenblum *et al.* On catalytic hydrogenation in aqueous ethanolic potassium hydroxide solution, XVI was quantitatively converted to the bridged ketone (VII; R = H) previously prepared by an alternative route. Hydrogenolysis also occurred in absence of base and the same product was obtained. Reduction of XVI using LAH and LAH-AlCl₃ afforded the dienol (XVIII) and diene (XIX) respectively. Both of these compounds were readily oxidized back to the dienone (XVI) with manganese dioxide showing that neither loss of chlorine nor double bond migration had occurred during these hydride reductions.

Treatment of XVI with concentrated sulphuric acid followed by hydrolysis gave [5]ferrocenophan-2-ene-1,5-dione (XX) which was converted to the known diketone (III; R = H) on hydrogenation. By a similar process, the diene (XIX) was converted to the $\beta\gamma$ -unsaturated ketone (XXI) and both this compound and XX gave [5]ferrocenophan-2-ene (XXII) on reduction with LAH-AlCl₃. Catalytic hydrogenation of XXII gave the parent [5]ferrocenophane (VI; R = H) while, on manganese dioxide oxidation, it was converted to a readily separable mixture of the unsaturated ketones XXI and XXIII, the latter predominating.

* A second compound, m.p. 157–158°, whose structure is under investigation, has been isolated from this reaction.



STRUCTURE AND CONFORMATION

The mass, IR, UV and PMR spectra of the [5]ferrocenophanes prepared in this study have been measured and have yielded information regarding the structure and conformation of these compounds. These results are discussed below and are compared with those of Rosenblum^{17,21} and Rinehart²² and their co-workers for the related [3] and [4] series.

Mass spectra. In common with most ferrocene derivatives,²³ the mass spectra of the [5]ferrocenophanes are characterized by the appearance of an intense group of molecular ion peaks arising from the presence of four naturally occurring iron isotopes. In a representative selection of compounds (see Experimental section), accurate mass measurement of the ^{56}Fe molecular ion permitted determination of molecular formulae which, in all cases, were consistent with the assigned structures. Fragmentation of these parent ions is limited and, in the case of the parent compound (VI; R = H), occurs by loss of CH_3 , C_2H_5 , C_3H_5 and C_4H_7 units. With the mono-

(VII; R = H) and diketone (III; R = H), on the other hand, loss of carbon monoxide occurs as a first step. Each of the above transitions was accompanied by the appearance of the appropriate metastable ion.

Infrared spectra. The values of the carbonyl stretching absorptions of the ketones prepared are given in the Experimental. In the case of all the [5]ferrocenophan-1-ones, effective conjugation between the carbonyl and cyclopentadienyl π -systems is apparent from the appearance of this band at even longer wavelengths (6.07 \pm 0.03 μ) than open-chain analogues (e.g. 1-acetyl-1'-ethylferrocene absorbs at 5.99 μ^{21}). This small bathochromic shift may be attributable to carbonyl valence angle deformation²⁴ induced by bridging strain. The sensitivity of the carbonyl absorption of [m]ferrocenophan-1-ones to conformational changes can be seen by comparing these values for the [3] (5.95 μ^{21}), [4] (6.07 μ^{21}) and [5] (6.09 μ) series. With increasing

TABLE I. UV SPECTRA *

Compound	Absorption maxima $\text{m}\mu$ ($\log \epsilon$)		
<i>Non-bridged ketones</i>			
Acetylferrocene	225 (4.22)	269 (3.80)	338 (3.10)
Acryloylferrocene	232*(4.10)	281 (3.87)	372 (3.21)
I	225 (4.32)	262 (4.10)	333 (3.25)
II (R = H)	230 (4.30)	280 (4.07)	364 (3.33)
V (R = H)	221 (4.35)	270 (4.08)	366 (3.23)
V (R = Ph)	223 (4.37)	264*(4.13)	309 (4.34) 365*(3.33)
1-Acetyl-1'-ethylferrocene ^b	228 (4.18)	270 (3.76)	340 (3.11)
<i>Bridged Monoketones</i>			
VII (R = H)	228*(4.12)	276 (3.67)	343 (3.11)
VII (R = Ph)	227*(4.15)	275 (3.67)	344 (3.16)
X	228 (4.15)	275 (3.70)	342 (3.16)
XI	228 (4.12)	275 (3.67)	342 (3.13)
XVI	234†(4.14)	263†(3.75)	308 (3.34) 344†(3.19)
XXI	230 (4.09)	276 (3.63)	345 (3.08)
XXIII	227*(4.07)	278 (3.63)	348 (3.15)
<i>Bridged diketones</i>			
III (R = H)	226 (4.36)	261 (3.97)	275†(3.74) 344 (3.29)
III (R = Ph)	227 (4.35)	252*(3.98)	276†(3.68) 348 (3.35)
IV	226 (4.41)	256 (4.00)	276†(3.74) 344 (3.29)
XX	224 (4.26)	260 (3.95)	277†(3.85) 304†(3.69) 344†(3.40)
<i>Unsaturated [5]ferrocenophanes</i>			
XII	224*(4.10)	275 (3.64)	340†(2.38)
XIII	222†(4.12)	274 (3.64)	340†(2.45)
XVIII	237*(3.81)	290 (3.43)	358†(2.59)
XIX	239*(3.82)	289 (3.52)	352†(2.74)
XXII	252†(3.58)		
<i>Saturated [5]ferrocenophanes</i>			
VI, VIII, IX, XV		249 \pm 4† (3.58 \pm 0.05)	

* In absolute EtOH unless otherwise indicated.

^b Ref. 25; in 95% EtOH.

* Shoulder.

† Inflection.

bridge length, conjugative overlap between carbonyl and ring π -orbitals can occur to a greater extent producing successive shifts to longer wavelength. Additional conjugation has only a small effect on the position of the ferrocenoyl (FcCO) band as shown by the values for acetyl- ($6.02\ \mu$), acryloyl- ($6.04\ \mu$) and cinnamoylferrocene ($6.06\ \mu$).

Ultraviolet spectra. The UV spectra of the compounds prepared are summarized in Table 1. As previously noted,^{21, 22} acylferrocenes show absorption maxima near 230 , 270 and $340\ \text{m}\mu$. It has been suggested^{21, 22} that the " $270\ \text{m}\mu$ " band is associated with electronic transitions involving ring-carbonyl molecular orbitals and that its position and intensity reflect the extent of conjugative interaction between these π -systems. The close correspondence between the spectra of [5]ferrocenophan-1-one (VII; $R = H$) and non-bridged models (e.g. 1-acetyl-1'-ethylferrocene²³) confirms (*vide supra*) that, in the former case, the carbonyl group can attain a conformation essentially in the plane of the cyclopentadienyl ring to which it is attached. A similar conclusion was reached²¹ in the case of the [4]analogue whereas, with [3]ferrocenophan-1-one, conjugation is substantially reduced.

Extension of conjugation of the ferrocenoyl group produces bathochromic shifts of all three absorption maxima. This effect is graphically illustrated by the curves for acetyl- and acryloylferrocene (Fig. 1). Since the spectra of the saturated and $\alpha\beta$ -unsaturated ketones (VII; $R = H$ and XXIII respectively) are very similar (Fig. 2), conjugation between the carbonyl group and adjacent double bond in XXIII must therefore be minimal, due to the constraint imposed on the 5-carbon bridge by the preferred inter-ring separation ($3.32\ \text{\AA}$ ²⁶) in the ferrocene nucleus.

Whereas those compounds with a saturated bridge (e.g. VI) fail to show any pronounced absorption maxima in the 220 – $300\ \text{m}\mu$ region, the unsaturated derivatives (XII and XIII) give well-defined maxima at $275\ \text{m}\mu$ which can be attributed to a $\pi \rightarrow \pi^*$ transition of the vinylferrocene chromophore. Conjugation of the cyclopentadienyl ring with an adjacent double bond is thus conformationally possible in the [5] series in contrast¹⁷ to the [3]. In the case of the diene (XIX) and dienol (XVIII), the $\pi \rightarrow \pi^*$ band is bathochromically shifted to $290\ \text{m}\mu$ indicating appreciable conjugation between the double bonds in the bridge. Predictably, the spectrum of [5]ferrocenophan-2-ene (XXII) is indistinguishable from that of the saturated parent (VI; $R = H$).

Proton magnetic resonance spectra. Details of the PMR spectra of the compounds prepared are included in the Experimental section. It has been suggested that the multiplicity of the ring proton resonance in the spectra of simple [m]ferrocenophanes indicates the extent of mutual ring tilt in these compounds.²⁷ It is generally accepted^{21, 22} that, in cases where bridging strain causes displacement of the cyclopentadienyl rings from parallel planes (e.g. [2]ferrocenophanes²⁸), those ring protons which lie closest to the iron atom will experience its shielding influence to the greatest extent. Alternatively, it can be argued that the magnitude of the shielding influence experienced by the individual ring protons in a ring-tilted ferrocene would be affected by orbital rehybridization at the iron atom,* since electron density would then be unsymmetrically disposed about a line connecting the metal atom with the centre of each ring.

* A molecular orbital treatment of the bonding in such a situation has been given.²⁹

The singlet resonances observed (CDCl_3 solution) for the ring protons of [3]^{21,22} and [4]ferrocenophane,²¹ therefore, infer that the interannular bridge causes little distortion of the ferrocene nucleus from its preferred "sandwich" geometry. By contrast, the ring protons of [5]ferrocenophane (VI; $R = H$) appear as a closely spaced multiplet (approximately two triplets; half height width ~ 4 c/s), suggesting either that ring tilt deformation of the ferrocene nucleus occurs during bridge inversion or, more probably, that conformational flexing of the bridge produces differential shielding of the α - and β -ring protons. The ring proton patterns for the mono- (VII; $R = H$) and diketone (III; $R = H$), on the other hand, approximate to those expected for non-bridged analogues. In the former case, the double triplet-single pattern typical³⁰ of an acylferrocene is observed whereas the latter compound gives rise to two clean triplets characteristic of a simple A_2B_2 system.

Whereas the methylene protons of VI and VII ($R = H$) appear as broad structureless multiplets, those of the diketone (III; $R = H$) give a sharp singlet. This can only be interpreted in terms of rapid inversion of the $-\text{CO}(\text{CH}_2)_3\text{CO}-$ bridge producing coincidence of the time-averaged chemical shifts of the associated protons. A similar situation obtains with [3]ferrocenophane and its 1-keto derivative.²² The spectra of the ethoxymethyl compounds (IV and IX) are particularly interesting in that the chemical shifts of the ethoxy protons are significantly influenced by the presence or otherwise of an adjacent carbonyl group and this distinction has enabled us to assign structures to the related isomeric ketones (X and XI). The chemical shifts of the methyl and methylene protons of the ethoxy group in these four derivatives are listed in Table 2 and it is apparent that the preferred conformations of IV and X involve location of the ethyl group within the shielding region of the adjacent carbonyl group.

TABLE 2. CHEMICAL SHIFTS OF ETHOXY PROTONS^a

Compound	τ_{CH_2} ^b	τ_{CH_3} ^b
IV	8.92	6.59
IX	8.80	6.49
X	8.89	6.58
XI	8.82	6.51

^a In CDCl_3 solution; TMS internal standard.

^b $J_{\text{CH}_2, \text{CH}_3} = 6.9$ c/s.

With the exception of the enol-acetate (XIII), whose vinyl proton appears as a sharp triplet ($J = 8.7$ c/s) at $\tau 4.61$, the spectra of the other unsaturated compounds contain complex multiplets in the vinyl region. The size of the coupling constant (10.9 c/s) between the vinyl protons of [5]ferrocenophan-1-ene (XII) confirms the expectation, based on inspection of molecular models,* that the double bond has a cis-stereochemistry.

* Dreiding ferrocene stereomodels supplied by W. Büchi, Glasapparatefabrik, Flawil, Switzerland were used.

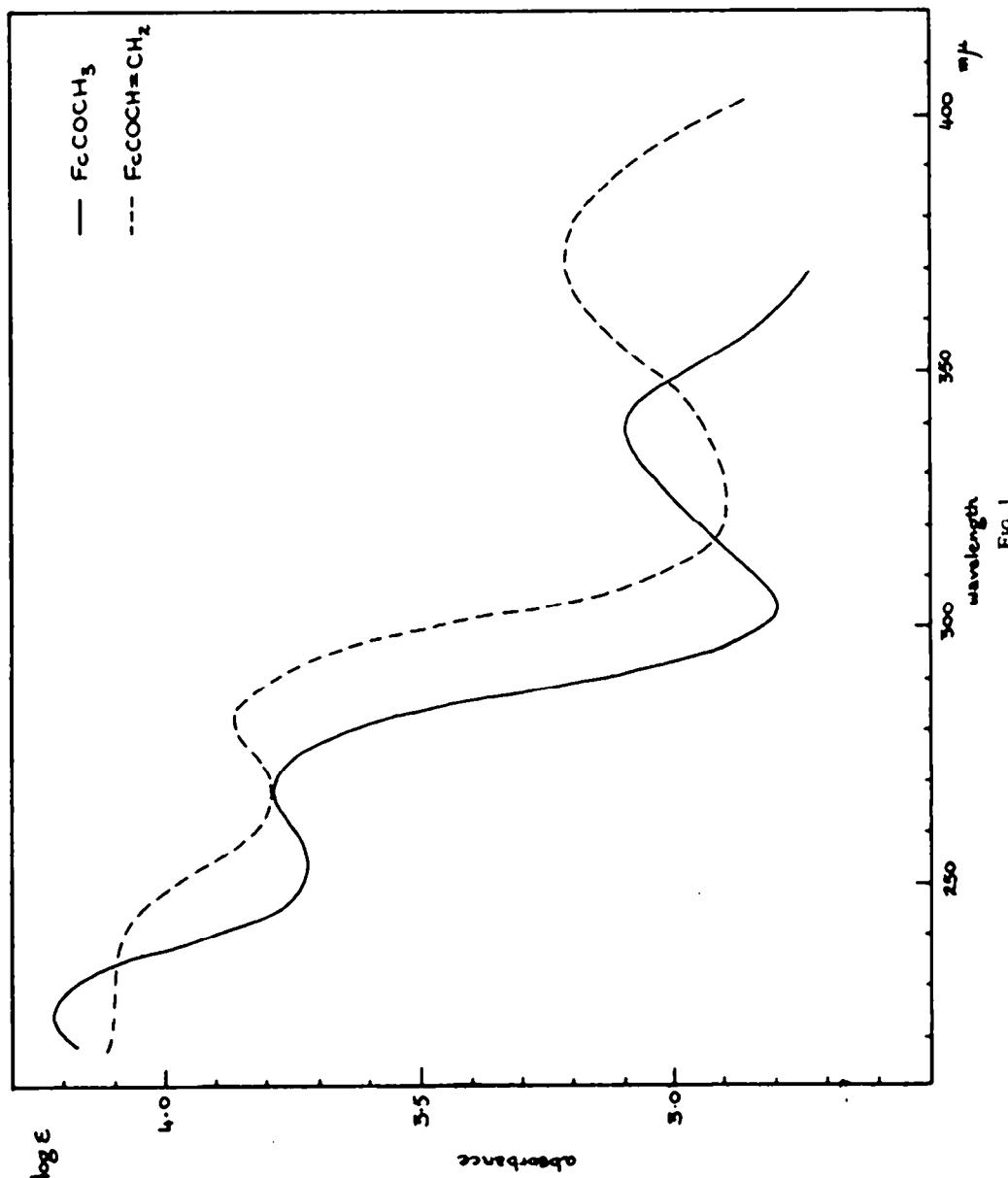


FIG. 1.

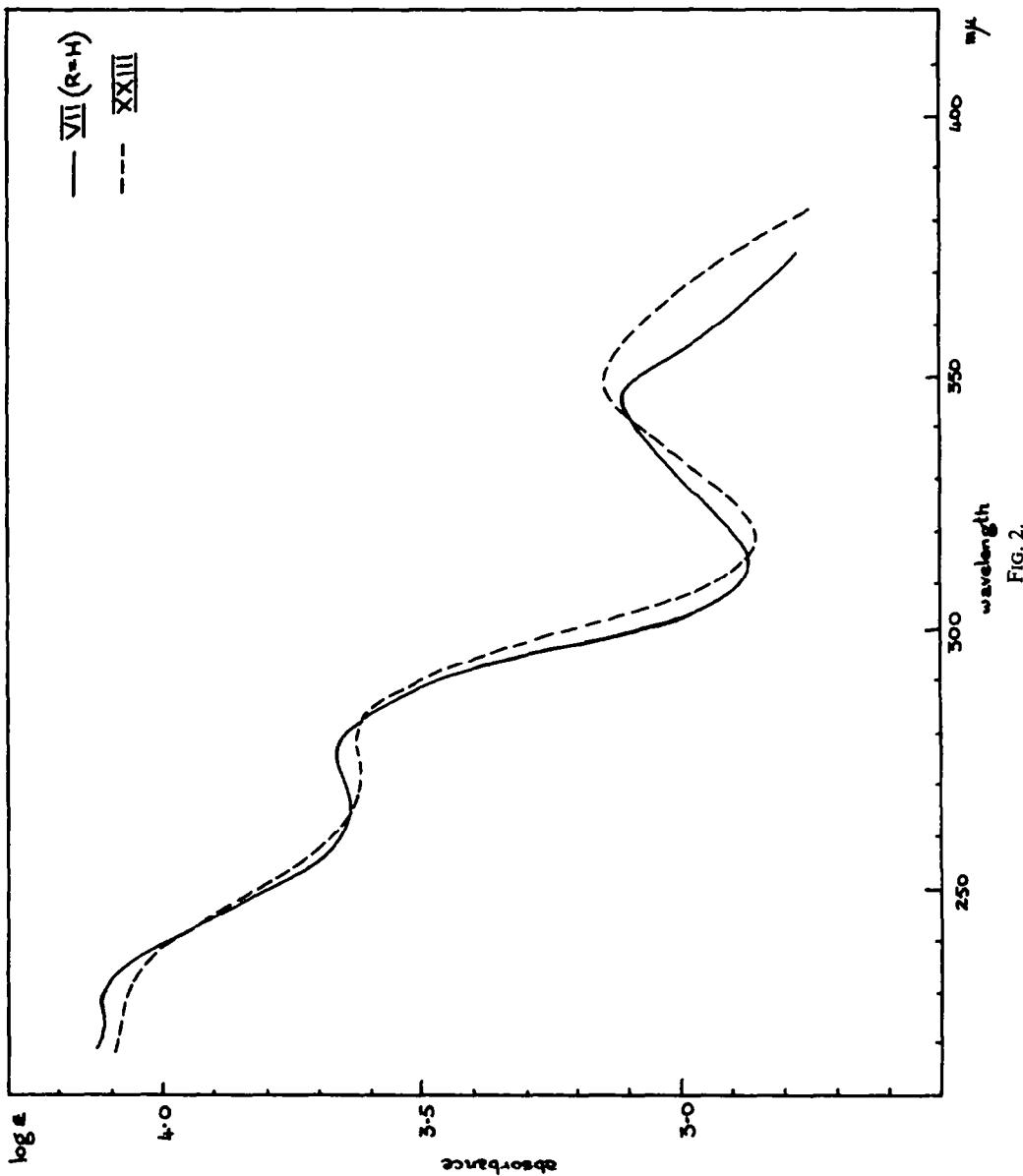


FIG. 2.

EXPERIMENTAL

IR spectra were recorded as Nujol mulls on a Perkin-Elmer 237 grating spectrometer and were individually calibrated against polystyrene film (6.24 μ); UV spectra on a Unicam SP800A recording spectrometer; PMR spectra in deuteriochloroform on a Perkin-Elmer R10 spectrometer at 40 Mc. using TMS as internal standard; mass spectra on an AEI MS9 spectrometer at 70 eV. Mol. wts were determined by accurate mass measurement of the ^{56}Fe molecular ion in the high resolution mass spectrum. Microanalyses were obtained by the University of Strathclyde microanalytical department under Dr. G. R. Proctor and by the Alfred Bernhardt microanalytical laboratory, Mulheim, West Germany. All reactions were carried out under an atmosphere of purified N_2 and yields of product are based on unrecovered starting material. M.ps were taken on a Kofler hot stage and are uncorrected. Ligroin refers to petrol b.p. 40–60°. Unless stated otherwise, chromatographies were carried out using Spence Grade H alumina which had been partially deactivated by exposure to the atmosphere. Neutral alumina was prepared by storing alumina under EtOAc for several days, filtering, washing with MeOH and water in turn, and drying at 160–170° for at least 4 hr. Acid alumina was prepared by storing alumina under conc HCl for several days, washing with water, and drying at 160–170° for at least 4 hr. Active MnO_2 was prepared according to the reported method.³¹

1-Acetyl-1'-acryloylferrocene (V; R = H)

A soln of the Perrier complex of β -chloropropionyl chloride was prepared by stirring a soln of the chloride (2.6 g; 0.02 mole) in CH_2Cl_2 (50 ml) with an excess of freshly ground AlCl_3 for 2 hr. The mixture was filtered and the filtrate was added with stirring to a soln of acetylferrocene (4.6 g; 0.02 mole) in CH_2Cl_2 (100 ml) over 20 min. The deep violet soln was stirred for 22 hr, then poured into water (600 ml). The organic phase was separated and combined with CH_2Cl_2 extracts of the aqueous phase. The total extract was washed with water, dried (Na_2SO_4), evaporated to low bulk, and chromatographed on neutral alumina. Benzene eluted unchanged acetylferrocene (2.8 g; 61% recovery). Benzene-ether eluted 1-acetyl-1'-acryloylferrocene (1.13 g; 51%), which crystallized from ligroin-benzene as a red solid, m.p. 60–61°. (Found: C, 63.92; H, 5.06. $\text{C}_{15}\text{H}_{14}\text{FeO}_2$ requires: C, 63.86; H, 5.00%); IR 6.02 μ ; PMR τ 2.65–4.43 (ABX pattern: 3H; vinyl protons), τ 5.06–5.61 (m; 8H; ring protons), τ 7.71 (s; 3H; Me protons).

1-Acetyl-1'-(β -chloropropionyl)ferrocene

The reaction between acetylferrocene (4.6 g; 0.02 mole) and the Perrier complex of β -chloropropionyl chloride (5.1 g; 0.04 mole) was carried out as described in the preceding experiment and the product was chromatographed on silica giving 1-acetyl-1'-(β -chloropropionyl)ferrocene (4.6 g; 73%), which crystallized from ligroin-ether as a red solid, m.p. 97–97.5°. (Found: C, 56.80; H, 4.93; Cl, 11.03. $\text{C}_{15}\text{H}_{15}\text{ClFeO}_2$ requires: C, 56.55; H, 4.75; Cl, 11.13%); IR 5.97, 6.01 μ ; PMR τ 5.20, 5.46 (2t; 8H; ring protons), τ 6.12 (m; 2H; COCH_2 protons), τ 6.89 (m; 2H; CH_2Cl protons), τ 7.68 (s; 3H; Me protons).

1,1'-Diacryloylferrocene (II; R = H)

A soln of ferrocene (3.72 g; 0.02 mole) in CH_2Cl_2 (40 ml) was added slowly to a soln of the Perrier complex of β -chloropropionyl chloride (5.1 g; 0.04 mole) in CH_2Cl_2 (200 ml). The deep violet soln was stirred for 5 hr and then poured into water (1000 ml). The organic phase was separated and combined with CH_2Cl_2 extracts of the aqueous phase. The total extract was washed with water, dried (Na_2SO_4), and evaporated. The orange brown residue was extracted with benzene and the insoluble material was crystallized from ligroin- CHCl_3 , giving 1,1'-di(β -chloropropionyl)ferrocene (0.27 g; 4%) as an orange yellow solid, m.p. 119–121° (lit.¹¹ 117–121°). The compound was recovered unchanged after chromatography on silica but underwent dehydrochlorination on neutral alumina giving 1,1'-diacryloylferrocene, identical to the product described below. The benzene-soluble material was chromatographed on neutral alumina. Ligroin eluted unchanged ferrocene (0.09 g; 3% recovery). Ligroin-ether (9:1) eluted acryloylferrocene (0.74 g; 16%), which crystallized from ligroin-ether as a red solid, m.p. 71–72° (lit.³² 73–74.5°); IR 6.04 μ ; PMR τ 2.75–4.5 (ABX pattern; 3H; vinyl protons), τ 5.18, 5.46 (2t; 4H; ring protons), τ 5.83 (s; 5H; ring protons). Ether eluted 1,1'-diacryloylferrocene (3.63 g; 64%), which was obtained as a deep red gum, unstable to heat and light, which could not be induced to crystallize. Satisfactory analytical data were not obtained; PMR τ 2.8–4.7 (ABX pattern; 6H; vinyl protons), τ 5.20, 5.48 (2t; 8H; ring protons). The compound was further characterized by hydrogenation in benzene soln over Pd-C to the known 1,1'-dipropionylferrocene, m.p. 52–53° (lit.³³ 52–54°).

1-Acetyl-1'-cinnamoylferrocene (V; R = Ph)

A soln of cinnamoyl chloride (6.7 g; 0.04 mole) in CH_2Cl_2 (40 ml) was added slowly with stirring to a mixture of acetylferrocene (4.6; 0.02 mole) and AlCl_3 (5.4 g; 0.04 mole) in CH_2Cl_2 (250 ml). The mixture was stirred for 4 hr, then carefully poured into ice-water (1000 ml) and the organic phase separated and combined with CH_2Cl_2 extracts of the aqueous phase. The total extract was washed with water, dried (Na_2SO_4), reduced to low bulk, and chromatographed on neutral alumina. Ligroin-ether (3:2) eluted acetyl ferrocene (1.2 g; 26% recovery) followed by a small orange band which afforded insufficient material for characterization. Ether eluted 1-acetyl-1'-cinnamoylferrocene (4.2 g; 80%), which crystallized from ligroin-ether as a red solid m.p. 131–132°. (Found: C, 70.13; H, 5.10. $\text{C}_{21}\text{H}_{18}\text{FeO}_2$ requires: C, 70.41; H, 5.07%); IR 5.99, 6.05 μ ; PMR τ 2.13, 2.99 (2d; 2H; vinyl protons; J = 15.5 c/s), τ 2.1–2.8 (m; 5H; Ph protons), τ 5.19, 5.21, 5.42, 5.49 (4t; 8H; ring protons), τ 7.66 (s; 3H; Me protons).

3-Phenyl[5]ferrocenophane-1,5-dione (III; R = Ph)

NaOH aq (1.5 g in 10% soln) was added slowly to a stirred soln of 1-acetyl-1'-cinnamoylferrocene (1.8 g; 5 mmole) in EtOH (150 ml) and the mixture was stirred for 12 hr, then diluted with water (500 ml) and extracted thoroughly with CH_2Cl_2 . The combined extracts were washed with water, dried (Na_2SO_4), concentrated to low bulk and chromatographed giving unchanged starting material (0.39 g; 22% recovery) followed by 3-phenyl[5]ferrocenophane-1,5-dione (0.97 g, 69%), which crystallized from benzene– EtOH as golden yellow feathers, m.p. > 300° (lit.^{5,6} > 300°); IR 6.03 μ ; the compound was identical to that prepared according to the directions³ of Hauser *et al.*

[5]Ferrocenophane-1,5-dione (III; R = H)

(a) The reaction between 1-acetyl-1'-acryloylferrocene (1.13 g; 4.0 mmole) in EtOH (100 ml) and NaOH aq (1.0 g in 10% soln) was carried out as in the preceding experiment and the product was chromatographed. Ether eluted [5]ferrocenophane-1,5-dione (0.99 g, 88%), which crystallized from ligroin-ether as an orange yellow solid, m.p. 251–253° (lit.⁸ 253°). (Found: M.W. 282-0335. $\text{C}_{15}\text{H}_{14}\text{FeO}_2$ requires: 282-0343); IR 6.03 μ ; PMR τ 5.18, 5.45 (2t; 8H; ring protons), τ 7.50 (s; 6H; methylene protons).

(b) The reaction between 1-acetyl-1'-(β -chloropropionyl) ferrocene (2.64 g; 8.3 mmole) in EtOH (150 ml) with NaOH aq (5.3 g in 10% soln) was carried out as in the preceding experiments and afforded III (R = H; 2.17 g; 93%), identical to the compound described under (a).

2-Ethoxymethyl[5]ferrocenophane-1,5-dione (IV)

(a) A soln of NaOEt (from 0.46 g Na, 20 mg at) in EtOH (10 ml) was added with stirring to a soln of 1,1'-diacryloylferrocene (0.80 g; 2.7 mmole) in EtOH (40 ml). The soln was stirred for 2 hr at room temp, then refluxed for 1 hr, cooled, diluted with water (500 ml) and extracted thoroughly with CHCl_3 . The combined extracts were washed with water, dried (Na_2SO_4), evaporated to low bulk, and chromatographed. Benzene–ether (7:3) eluted 2-ethoxymethyl[5]ferrocenophane-1,5-dione (0.83 g; 89%), which crystallized from ligroin–benzene as orange yellow needles, m.p. 140–142°. (Found: C, 63.63; H, 5.76; M.W. 340-0759. $\text{C}_{18}\text{H}_{20}\text{FeO}_3$ requires: C, 63.54; H, 5.93%; M.W. 340-0761); IR 6.02 μ ; PMR τ 5.0–5.6 (m; 8H; ring protons), τ 6.55 (bs; 3H; COCH_2O protons), τ 6.59 (q; 2H; ethoxy methylene protons), τ 7.59 (bs; 4H; bridge protons), τ 8.93 (t; 3H; Me protons).

(b) An aqueous soln (40%) of formaldehyde (5.4 g; 0.18 mole) was added dropwise with stirring to a soln of 1,1'-diacetylferrocene (24 g; 0.09 mole) in a mixture of EtOH (350 ml) and NaOH aq (10%; 42 ml). The mixture was stirred for 16 hr, then diluted with water (1000 ml) and extracted thoroughly with CHCl_3 . The combined extracts were washed with water, dried (Na_2SO_4), and evaporated. The residual brown solid was dissolved in benzene and chromatographed. Ligroin-ether mixtures eluted three bands which did not separate cleanly. After further chromatographic purification, the following compounds (in order of elution) were obtained: 1,1'-diacetylferrocene (2.75 g; 11.5% recovery); 2-ethoxymethyl[5]ferrocenophane-1,5-dione (6.85 g; 31%), identical to the compound described under (a); [5]ferrocenophane-1,5-dione (2.85 g; 13%), identical to the compound described in a previous experiment.

[5]Ferrocenophane (VI; R = H)

A mixture of III (R = H; 0.564 g; 2 mmole), LAH (0.35 g; 10 mmole) and freshly ground AlCl_3 (2.0 g; 15 mmole) in dry ether (60 ml) was stirred under reflux for 3 hr. The excess of hydride was destroyed by addition of moist ether and the reaction mixture was poured into water (500 ml). The organic phase was separated and combined with ether extracts of the aqueous phase. The total extract was washed with water,

dried (Na_2SO_4) and evaporated and the residual liquid was dissolved in ligroin and chromatographed. Ligroin eluted [5]ferrocenophane (0.437 g; 86%), which crystallized from ligroin as a yellow solid, m.p. 60–61° (lit.¹⁴ 60–61°). (Found: C, 71.08; H, 7.32; M.W. 254.0757. $\text{C}_{15}\text{H}_{18}\text{Fe}$ requires: C, 70.91; H, 7.14%; M.W. 254.0757); PMR τ 5.8–6.1 (m; 8H; ring protons), τ 7.4–8.4 (m; 10H; methylene protons).

3-Phenyl[5]ferrocenophane (VI; R = Ph)

The hydride reduction of III (R = Ph; 0.43 g; 1.2 mmole) was carried out as described in the preceding experiment and the product chromatographed. Ligroin eluted 3-phenyl[5]ferrocenophane (0.34 g; 86%), which crystallized from ligroin as a yellow solid, m.p. 112–113° (lit.¹⁵ 110–112°). (Found: C, 76.38; H, 6.69; M.W. 330.1064. $\text{C}_{18}\text{H}_{22}\text{Fe}$ requires: C, 76.37; H, 6.71%; M.W. 330.1070); PMR τ 2.7 (s; 5H; Ph protons), τ 5.6–6.0 (m; 9H; ring and methine protons), τ 7.4–8.3 (m; 8H; methylene protons).

2-Ethoxymethyl[5]ferrocenophane (IX)

The hydride reduction of IV (0.60 g; 1.76 mmole) was carried out as described previously and afforded 2-ethoxymethyl[5]ferrocenophane (0.45 g; 82%), which was distilled as an orange yellow liquid, b.p. 170° (bath)/0.1 mm. (Found: C, 69.02; H, 8.21. $\text{C}_{18}\text{H}_{24}\text{FeO}$ requires: C, 69.23; H, 7.75%); PMR τ 5.99 (bs; 8H; ring protons), τ 6.49 (q; 2H; ethoxy methylene protons), τ 6.7 (bs; 2H; CH_2O protons), τ 7.3–8.3 (m; 9H; bridge protons), τ 8.8 (t; 3H; Me protons).

3-Phenyl[5]ferrocenophan-1-one (VII; R = Ph)

A soln of 3-phenyl[5]ferrocenophane (0.40 g; 1.2 mmole) in benzene (15 ml) was heated with MnO_2 (2 g) at 60° for 2 hr. The solid was filtered off, washed with benzene and the filtrate and washings were combined, evaporated to low bulk, and chromatographed. Ligroin–ether eluted 3-phenyl[5]ferrocenophan-1-one (0.237 g, 68%), which crystallized from ligroin–benzene as fine yellow needles, m.p. 169–171°. (Found: C, 73.11; H, 5.91; M.W. 344.0864. $\text{C}_{18}\text{H}_{20}\text{FeO}$ requires: C, 73.26; H, 5.86%; M.W. 344.0863); IR 6.10 μ ; PMR τ 2.7 (s; 5H; phenyl protons), τ 5.0–6.0 (m; 9H; ring and methine protons), τ 7.0–8.3 (m; 6H; methylene protons).

2- and 4-Ethoxymethyl[5]ferrocenophan-1-one (X and XI respectively)

MnO_2 oxidation of 2-ethoxymethyl[5]ferrocenophane (2.0 g; 6.4 mmole) was carried out as described previously and the product was chromatographed. Ligroin eluted unchanged starting material (0.63 g; 31.5% recovery). Ligroin–ether (9:1) eluted 2-ethoxymethyl[5]ferrocenophan-1-one (0.085 g; 6%), which was distilled as an orange yellow liquid, b.p. 190° (bath)/0.1 mm. (Found: C, 66.68; H, 6.73. $\text{C}_{18}\text{H}_{22}\text{FeO}_2$ requires: C, 66.27; H, 6.75%); IR 6.04 μ (liquid film); PMR τ 5.23, 5.51 (2t; 4H; ring protons), τ 5.93 (s; 4H; ring protons), τ 6.2–6.9 (m; 5H; $\text{CHCH}_2\text{OCH}_2$ protons), τ 7.5–8.4 (m; 6H; bridge methylene protons), τ 8.89 (t; 3H; Me protons). Ligroin–ether (9:1) then eluted 4-ethoxymethyl[5]ferrocenophan-1-one (0.52 g; 37%), which crystallized from ligroin–ether as an orange yellow solid, m.p. 63–64°. (Found: C, 66.33; H, 6.71. $\text{C}_{18}\text{H}_{22}\text{FeO}_2$ requires: C, 66.27; H, 6.75%); IR 6.08 μ ; PMR τ 5.1–5.6 (m; 4H; ring protons); τ 5.7–6.0 (m; 4H; ring protons), τ 6.51 (q; 2H; ethoxy methylene protons), τ 6.7 (bs; 2H; CH_2O protons), τ 7.1–8.2 (m; 7H; bridge protons), τ 8.82 (t; 3H; Me protons).

[5]Ferrocenophan-1-ol (VIII; R = H)

A solution of VII (R = H; 0.35 g; 1.3 mmole) in dry ether (20 ml) was added to a stirred suspension of LAH (0.35 g; 10 mmole) in dry ether (40 ml) and the mixture was stirred for 16 hr. The excess of hydride was destroyed by addition of moist ether and the mixture was poured into water (300 ml). The organic phase was separated and combined with ether extracts of the aqueous phase. The total extract was washed with water, dried (Na_2SO_4), concentrated to low bulk and chromatographed. Ligroin–ether eluted unchanged starting material (0.034 g, 10% recovery). Ether eluted [5]ferrocenophan-1-ol (0.275 g; 88%), which crystallized from ligroin–ether as an orange-yellow solid, m.p. 108–109.5°. (Found: C, 66.87; H, 6.58. $\text{C}_{15}\text{H}_{18}\text{FeO}$ requires: C, 66.67; H, 6.67%); PMR τ 5.2–5.6 (m; 1H; methine proton), τ 5.7–6.2 (m; 8H; ring protons), τ 7.4–8.6 (m; 8H; methylene protons), τ 8.26 (s; 1H; OH proton).

3-Phenyl[5]ferrocenophan-1-ol (VIII; R = Ph)

Hydride reduction of VII (R = Ph; 0.20 g; 0.58 mmole) was carried out as in the preceding experiment and the product was chromatographed. Ether eluted 3-phenyl[5]ferrocenophan-1-ol (0.14 g; 70%), which crystallized from ligroin–ether as an orange yellow solid, m.p. 119–121°. (Found: C, 72.59; H, 6.29.

$C_{21}H_{22}FeO$ requires: C, 72.82; H, 6.41%; PMR τ 2.68 (s; 5H; Ph protons), τ 5.4–5.7 (m; 1H; CHOH proton), τ 5.6–6.2 (m; 9H; ring and benzylic protons); τ 7.4–8.4 (m; 6H; methylene protons), τ 8.37 (s; 1H; OH proton).

[5]Ferrocenophan-1-ene (XII)

$POCl_3$ (0.3 g; 2 mmole) was added dropwise with stirring to an ice-cold soln of VIII ($R = H$; 0.4 g; 1.5 mmole) in pyridine (40 ml). After 15 min at 0°, the mixture was heated to 80–90° for 6 hr, then cooled, diluted with water (400 ml) and extracted with ether. The combined extracts were washed with dil HCl aq then with water, dried (Na_2SO_4) evaporated to low bulk and chromatographed. Ligroin eluted [5]ferrocenophan-1-ene (0.32 g, 86%), which crystallized from ligroin as an orange yellow solid, m.p. 90–91°. (Found: C, 71.32; H, 6.27. $C_{15}H_{16}Fe$ requires: C, 71.46; H, 6.35%); PMR τ 3.78 (d; 1H; vinyl proton), τ 4.05–4.75 (m; 1H; vinyl proton), τ 5.90, 5.99 (2s; 4H and 4H; ring protons), τ 6.95–8.8 (m; 6H; methylene protons).

1-Acetoxy[5]ferrocenophan-1-ene (XIII)

A soln of VII ($R = H$; 0.5 g; 1.9 mmole) and toluene-*p*-sulphonic acid (0.1 g) in isopropenyl acetate (40 ml) was refluxed for 67 hr. The solvent was then evaporated under reduced press and the brown residue was extracted with ether. The combined extracts were washed with 5% $NaHCO_3$ aq till free from acid, then with water, dried (K_2CO_3), reduced to low bulk and chromatographed on silica. Ligroin–ether (9:1) eluted 1-acetoxy[5]ferrocenophan-1-ene (0.32 g, 86%), which crystallized from ligroin–ether as long yellow needles, m.p. 76–77°. (Found: C, 66.06; H, 5.83. $C_{17}H_{18}FeO_2$ requires: C, 65.80; H, 5.81%); PMR τ 4.62 (t; 1H; vinyl proton; $J = 8.6$ c/s), τ 5.71, 5.85 (2t; 4H; ring protons), τ 5.93 (s; 4H; ring protons), τ 6.95–8.6 (m; 6H; methylene protons), τ 7.93 (s; 3H; Me protons).

Tetrahydropyranyl derivative (XV; $R = H$)

A soln of III ($R = H$; 0.75 g; 2.66 mmole) in dry THF (40 ml) was added to a stirred suspension of LAH (0.70 g, 20 mmole) in dry THF (80 ml) and the mixture was heated under reflux for 4 hr then cooled. The excess of hydride was destroyed by addition of moist ether and the mixture was poured into water (600 ml). The organic phase was separated and combined with ether extracts of the aqueous phase. The total extract was washed with water, dried (Na_2SO_4) and evaporated and the residue was dissolved in benzene and chromatographed. Ligroin eluted the ether (XV; $R = H$; 0.42 g, 59%), which crystallized from ligroin–ether as an orange yellow solid, m.p. 166.5–167.5°. (Found: C, 67.18; H, 5.94; M.W. 268.0551. $C_{15}H_{16}FeO$ requires: C, 67.19; H, 6.02%; M.W. 268.0550); PMR τ 5.4–5.8 (m; 2H; methine protons), τ 5.75–6.0 (m; 8H; ring protons), τ 7.6–8.6 (m; 6H; methylene protons). Two other minor products, showing both CO and OH IR absorption, were eluted by ether (+5% MeOH) but were not characterized due to lack of material.

Tetrahydropyranyl ethers (XV; $R = Ph$)

Hydride reduction of III ($R = Ph$; 1.8 g; 5 mmole) was carried out as in the preceding experiment and the product was chromatographed. Ligroin–ether eluted the ether (XV; $R = Ph$; 0.43 g; 25%), which crystallized from ligroin–ether as an orange yellow solid, m.p. 167–169°. (Found: C, 72.94; H, 5.81; M.W. 344.0864. $C_{21}H_{20}FeO$ requires: C, 73.26; H, 5.86%; M.W. 344.0863); PMR τ 2.70 (s; 5H; phenyl protons), τ 5.20–5.50 (bt; 2H; CHOCH protons), τ 5.6–5.9 (m; 8H; ring protons), τ 6.0–6.9 (m; 1H; benzylic proton), τ 7.6–8.1 (m; 4H; methylene protons). Ether (+5% MeOH) eluted a gummy orange yellow solid (0.69 g) which could not be crystallized but whose IR spectrum showed OH but no CO or ether absorption. A soln of this material in CH_2Cl_2 (60 ml) was shaken with acid alumina (25 g) for 16 hr. The alumina was then filtered off, washed with CH_2Cl_2 and the filtrate was evaporated to dryness affording a second ether (XV; $R = Ph$; 0.27 g, 16%), which crystallized from ligroin–ether as an orange yellow solid, m.p. 163–164.5°. (Found: C, 72.78; H, 5.64; M.W. 344.0862. $C_{21}H_{20}FeO$ requires: C, 73.26; H, 5.86%; M.W. 344.0863); the spectral properties of this compound were very similar to those of the first isomer.

1-Chloro[5]ferrocenophane-1,3-dien-5-one (XVI)

This compound was prepared according to the method²⁰ of Rosenblum *et al.* from the unsaturated aldehyde XVII. In the preparation of this precursor (XVII), however, it was found necessary to increase the $POCl_3$ –1,1'-diacetylferrocene ratio to twice the reported value. Under the conditions described,²⁰ the main product of the reaction was 1,1'-di(α -chlorovinyl)-ferrocene and only trace amounts of XVII were isolated.

1-Chloro[5]ferrocenophane-1,3-dien-5-ol (XVIII)

A soln of XVI (0.60 g; 2 mmole) in dry ether (20 ml) was added dropwise to a suspension of LAH (0.28 g; 8 mmole) in dry ether (40 ml) and the mixture was stirred for 4 hr. The excess of hydride was destroyed by addition of moist ether and the mixture was poured into water (250 ml). The organic phase was separated and combined with ether extracts of the aqueous phase and the total extract was washed with water, dried (Na_2SO_4), concentrated to low bulk and chromatographed. Ether eluted 1-chloro[5]ferrocenophane-1,3-dien-5-ol (0.40 g; 66%), which crystallized from ligroin-ether as chunky orange prisms, m.p. 129.5–130.5°. (Found: C, 60.13; H, 4.41; Cl, 11.81. $\text{C}_{15}\text{H}_{13}\text{ClFeO}$ requires: C, 59.93; H, 4.36; Cl, 11.80%); PMR τ 3.7–4.3 (m; 3H; vinyl protons), τ 4.84 (bd; 1H; methine proton), τ 5.3–6.0 (m; 8H; ring protons), τ 7.95 (bs; 1H; OH proton). This compound was readily oxidized back to XVI in 92% yield by the action of MnO_2 in CHCl_3 according to the procedure previously described.

1-Chloro[5]ferrocenophane-1,3-diene (XIX)

The reaction of XVI (1.5 g; 5 mmole), LAH (0.70 g; 20 mmole) and AlCl_3 (5.34 g; 40 mmole) was carried out as described previously and the product was chromatographed. Ligroin eluted 1-chloro[5]ferrocenophane-1,3-diene (1.20 g; 84%), which crystallized from ligroin-ether as an orange solid, m.p. 80–81°. (Found: C, 63.56; H, 4.88. $\text{C}_{15}\text{H}_{13}\text{ClFe}$ requires: C, 63.32; H, 4.61%); PMR τ 3.7–4.3 (m; 3H; vinyl protons), τ 5.60, 5.83, 5.86, 5.99 (4t; 8H; ring protons), τ 7.05–7.35 (m; 2H; methylene protons). This compound was oxidized back to XVI by MnO_2 in CHCl_3 following the normal procedure.

[5]Ferrocenophan-2-ene-1,5-dione (XX)

The dienone XVI (0.60 g; 2 mmole) was added slowly with vigorous stirring to conc H_2SO_4 (20 ml). The dark green soln was stirred for 0.5 hr and then poured into ice-cold water (500 ml). The soln was stirred for a further 0.5 hr and then extracted with CH_2Cl_2 . The combined extracts were washed with NaHCO_3 aq then with water, dried (Na_2SO_4), concentrated to low bulk and chromatographed. Ether eluted [5]ferrocenophan-2-ene-1,5-dione (0.45 g; 74%), which crystallized from ligroin-ether as an orange red solid, m.p. 220–222°. (Found: C, 63.98; H, 4.31. $\text{C}_{15}\text{H}_{12}\text{FeO}_2$ requires: C, 64.32; H, 4.32%); IR 6.03 μ ; PMR τ 3.7–4.3 (m; 2H; vinyl protons), τ 5.21, 5.40 (2t; 8H; ring protons), τ 6.55–6.75 (m; 2H; methylene protons). This compound underwent ready conversion to III (R = H) previously described on hydrogenation in benzene soln over Pt catalyst.

[5]Ferrocenophan-3-en-1-one (XXI)

Following the same procedure as in the preceding experiment, XIX (0.5 g; 1.76 mmole) was converted to [5]ferrocenophan-3-en-1-one (0.21 g; 47%), which crystallized from ligroin-ether as an orange yellow solid, m.p. 118.5–120°. (Found: C, 67.83; H, 5.32. $\text{C}_{15}\text{H}_{14}\text{FeO}$ requires: C, 67.70; H, 5.31%); IR 6.08 μ ; PMR τ 3.8–4.6 (m; 2H; vinyl protons), τ 5.30, 5.52 (2t; 4H; ring protons), τ 5.91 (s; 4H; ring protons), τ 6.60–6.83 (m; 2H; C_2 methylene protons), τ 6.85–7.17 (m; 2H; C_5 methylene protons).

[5]Ferrocenophan-2-ene (XXII)

(a) The reaction between XX (1.40 g; 5 mmole), LAH (1.36 g; 40 mmole) and AlCl_3 (6.67 g; 50 mmole) was carried out as described in previous experiments and the product was chromatographed. Ligroin eluted [5]ferrocenophan-2-ene (0.90 g; 72%), which crystallized from ligroin as pale yellow plates, m.p. 56.5–57.5°. (Found: C, 71.12; H, 6.25. $\text{C}_{15}\text{H}_{16}\text{Fe}$ requires: C, 71.46; H, 6.35%); PMR τ 3.9–4.45 (m; 2H; vinyl protons), τ 5.97 (s; 8H; ring protons), τ 6.98 (d; 2H; C_1 methylene protons), τ 7.4–7.9 (bs; 4H; C_4 and C_5 methylene protons).

(b) Reduction of XXI (50 mg; 0.19 mmole) was carried out as described under (a) and afforded [5]ferrocenophan-2-ene (40 mg; 80%), m.p. 56–57°, identical to the compound previously obtained.

Hydrogenation of XXII in benzene soln over Pt catalyst afforded [5]ferrocenophane, identical to the compound previously described.

[5]Ferrocenophan-2-en-1-one (XXIII)

A soln of [5]ferrocenophan-2-ene (0.45 g; 1.8 mmole) in benzene (15 ml) was shaken with active MnO_2 (5 g) for 21 hr. The reaction was worked up as described in a previous experiment and the product was chromatographed. Ligroin eluted unchanged starting material (85 mg; 19% recovery). Ligroin-ether (4:1) eluted [5]ferrocenophan-3-en-1-one (0.12 g; 31%), identical to the compound obtained in a previous experiment. The same solvent then eluted [5]ferrocenophan-2-en-1-one (0.23 g; 60%), which crystallized

from ligroin-ether as an orange solid, m.p. 121.5-123%. (Found: C, 67.59; H, 5.35. $C_{15}H_{14}FeO$ requires: C, 67.70; H, 5.31%); IR 6.10 μ ; PMR τ 3.5-4.6 (m; 2H; vinyl protons), τ 5.26, 5.47 (2t; 4H; ring protons), τ 5.92 (s; 4H; ring protons) τ 6.47, 6.54 (2bs; 4H; methylene protons).

[5]Ferrocenophan-1-one (VII; R = H)

(a) A soln of [5]ferrocenophane (0.382 g; 1.5 mmole) in $CHCl_3$ (15 ml) was left in contact with active MnO_2 (2 g) for 66 hr with occasional shaking. The solid was filtered off and washed with $CHCl_3$, and the filtrate and washings were combined, evaporated to low bulk, and chromatographed. Ligroin eluted unchanged starting material (43 mg; 11% recovery). Ligroin-ether eluted [5]ferrocenophan-1-one (0.262 g; 73%), which crystallized from ligroin-ether as fine yellow needles, m.p. 123.5-124.5°. (Found: C, 67.16; H, 6.04; M.W. 268.0544. $C_{15}H_{16}FeO$ requires: C, 67.19; H, 6.02%; M.W. 268.0550); IR 6.09 μ ; PMR τ 5.28, 5.52 (2t; 4H; ring protons), τ 5.92 (s; 4H; ring protons), τ 7.2-8.3 (m; 8H; methylene protons).

(b) A soln of XVI (0.6 g; 2 mmole) in a mixture of $MeOH$ (60 ml) and 10% $KOHaq$ (6 ml) was hydrogenated in presence of $Pd-C$ (10% Pd; 0.25 g). When uptake of H_2 had ceased, the soln was filtered and the filtrate was diluted with water (250 ml) and extracted with ether. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated giving [5]ferrocenophan-1-one (0.48 g; 90%), identical to the compound described under (a).

(c) Similarly, hydrogenation of either XVI or XXIII in benzene soln in presence of Pt catalyst gave [5]ferrocenophan-1-one, identical to the compound described under (a). In the former case, traces of [5]ferrocenophane were also isolated.

Acknowledgements—The authors thank Drs. G. R. Proctor and P. Bladon and their staffs for microanalyses and spectra, Miss E. S. Bolton for technical assistance, Arapahoe Chemicals, Inc., for generous gifts of ferrocene, and the Science Research Council for a maintenance grant (to T.H.B.).

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²⁷ A summary of the published data and leading Refs. are contained in Ref. 2, p. 250.

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