Stable Carbonium Ions. Part VII.[1] Cycloaddition Reactions of Ferrocenylalkylium Ions with Cyclopentadiene

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The reaction of ferrocenylalkylium ions with cyclopentadiene proceeds stereoselectively to give 1 : 1 cycloaddition products which incorporate a bicyclo[3.2.1]oct-6-ene skeleton fused to a cyclopentadienyl ring (giving a methanoazulenyl structure). Both stereoisomeric forms of (π-cyclopentadienyl)[η-1—3a(8a)-4,7-methano-7,8-dihydro-4*H*-azulenyl]iron(II) have been synthesised from *cis*-3-ferrocenylcyclopentanecarboxylic acid. The stereochemical features of the cycloaddition reactions have been established from the ^{1}H n.m.r. spectral properties of the products and their derivatives.

In recent years, evidence has accumulated to suggest that the reaction pathways followed by π-hydrocarbons in orbital symmetry controlled reactions may be diverted when the hydrocarbon functions as a ligand to a transition metal.[2] In such complexes, mixing of the ligand orbitals with those of the metal serves to modify the energy requirements for pericyclic processes such that

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[1] Part VI, T. D. Turbitt and W. E. Watts, preceding paper.

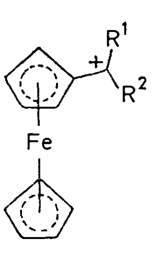
[2] B. T. Golding and A. P. Johnson, *Ann. Reports* (*B*), 1970, **67**, 399; 1971, **68**, 351.

reactions may be observed which are disfavoured in the metal-free system.[3]

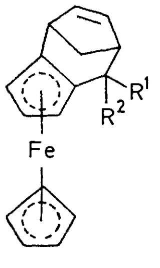
Ferrocenylalkylium ions (1) may be thought of as π-complexed fulvenes with a cationic (π-cyclopentadienyl)iron residue. Although recent work[4] has strongly suggested that the fulvene ligands of such cations may be grossly distorted from the planar geometry adopted by the uncomplexed hydrocarbons, nevertheless it appeared of interest to investigate the effect of metal complexation upon the course of cycloaddition reactions of fulvenes with π-hydrocarbons.[5] Although fulvenes themselves normally function as 2π- or 4π-electron addends in [4*s* + 2*s*] cycloadditions[6] (*e.g.*, Diels–Alder dimerisation of dialkylfulvenes[7]), an example of a [6*s* + 4*s*] process has recently been described[8] in which 6,6-dimethylfulvene apparently acts as a 6π-electron addend in a cycloaddition reaction with tropone.

Cations of the type (1) are normally generated by the reaction of alkenylferrocenes or 1-hydroxyalkylferrocenes with strong protic acids.[1] However, cycloadditions of the type envisaged require aprotic media in order to avoid undesired side-reactions. This difficulty has been circumvented by employing trityl tetrafluoroborate ($Ph_3C^+BF_4^-$) which in dichloromethane quantitatively abstracts the hydroxy-group of the alcohols generating stable solutions of the corresponding cations. The procedure is successful for the preparation of secondary and tertiary carbonium ions [*e.g.*, (1a and b)] but ferrocenylmethanol undergoes dehydration under these conditions to give bis(ferrocenylmethyl) ether ($FcCH_2OCH_2$-Fc).

Treatment *in situ* of the cation (1a), generated from 2-ferrocenylpropan-2-ol by this method, with a large excess of cyclopentadiene gave a mixture of six products which was separated by repeated chromatography on alumina. Three of the products were identified as the alkenylferrocenes (5)—(7) and two as the bridged ferrocenes (8) and (9). Previous workers have shown[9] that the last four compounds are formed from the cation (1d) by proton elimination or internal electrophilic substitution, and that this cation results from the addition of the parent cation (1a) to isopropenylferrocene (5). We established in a separate experiment that compounds (5)—(9) are formed when the original reaction is carried out in the absence of cyclopentadiene. The molecular formula ($C_{18}H_{20}Fe$; mass spectrum) of the sixth product of the original reaction (*ca.* 12% yield) showed that it resulted from a 1 : 1 addition of the cation (1a) and cyclopentadiene, followed by deprotonation. The structure (2a) was indicated by the ^1H n.m.r. spectrum of the compound. In particular, the marked non-equivalence of the methyl groups (τ 8·4 and 9·1) demands a structure in which these groups are held in different stereochemical locations within the local diamagnetic field associated with the ferrocene residue.[10]



(1)



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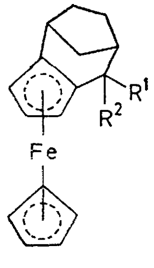
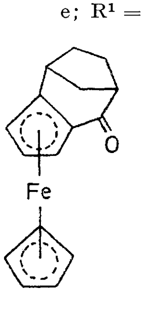


(3)

a; $R^1 = R^2 = Me$
b; $R^1 = Me$; $R^2 = H$
c; $R^1 = R^2 = H$
d; $R^1 = Me$; $R^2 = CH_2CMe_2Fc$
e; $R^1 = H$; $R^2 = CH_2CHMeFc$



(4)

$FcCMe{=}CH_2$

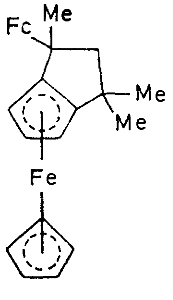
(5)

$FcCMe_2CH{=}CMeFc$

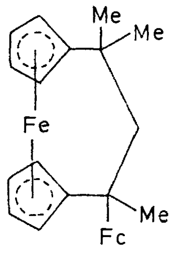
(6)

$FcCMe_2CH_2CFc{=}CH_2$

(7)



(8)



(9)

The secondary cation (1b), formed by hydroxide abstraction from 1-ferrocenylethanol, underwent a similar reaction with cyclopentadiene to give a low yield of the 1 : 1 addition product (2b). The complex mixture of oligomeric by-products, presumably derived from the cation (1e), was not separated or investigated. The parent compound (2c) of the series was obtained from the reaction of chloromethylferrocene with cyclopentadiene in dichloromethane. This reaction no doubt involves heterolysis of the extremely weak C–Cl bond of the

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[3] *E.g.* V. Aris, J. M. Brown, and B. T. Golding, *J.C.S. Chem. Comm.*, 1972, 1206; M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *J.C.S. Perkin II*, 1972, 1141.

[4] S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1025; T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 185.

[5] Preliminary communication; T. D. Turbitt and W. E. Watts, *Chem. Comm.*, 1971, 631.

[6] E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41.

[7] K. Alder and G. Stein, *Annalen*, 1932, **496**, 204.

[8] K. N. Houk, L. J. Luskus, and N. S. Bhacca, *J. Amer. Chem. Soc.*, 1970, **92**, 6392; *Tetrahedron Letters*, 1972, 2297.

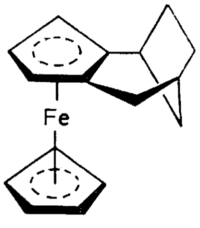
[9] (*a*) W. M. Horspool, R. G. Sutherland, and J. R. Sutton, *Canad. J. Chem.*, 1969, **47**, 3085; (*b*) W. M. Horspool, P. Stanley, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc.* (*C*), 1971, 1365.

[10] T. D. Turbitt and W. E. Watts, *Tetrahedron*, 1972, **28**, 1227.

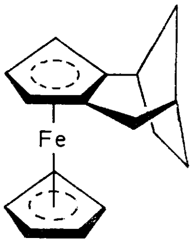
chloride,[11] followed by capture of the diene by the intermediate primary cation (1c).

The presence of one double bond in these addition products was confirmed by catalytic hydrogenation of (2a and c) which proceeded with uptake of equimolar amounts of hydrogen to give the corresponding saturated compounds (3a and c). Oxidation of product (3c) with ' active ' manganese dioxide afforded the saturated ketone (4). The cyclopentadienyl proton resonance pattern in the ^{1}H n.m.r. spectrum of this ketone (see Experimental section) was entirely consistent with its formulation as an (α-acyl)alkylferrocene. From these results and from the striking similarities in the ^{1}H n.m.r. spectra of the three addition products, it may be assumed that they belong to the same structural series.

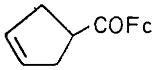
Ferrocene derivatives of the types (2)—(4) can exist in two different stereoisomeric forms, each a racemate, depending upon the mode of fusion of the ferrocene residue. In order to establish the stereochemistry of products (2) of the cyclopentadiene addition reactions, the syntheses of the two forms (10A and B) of the saturated derivative (3c) and the corresponding stereoisomers of the ketone (4) were planned. As a first approach, 4-ferrocenoylcyclopentene (11) was prepared by Friedel–Crafts acylation of ferrocene using 4-(chlorocarbonyl)-cyclopentene, and this ketone was converted into the ferrocenylmethyl derivative (12) by mixed-hydride reduction. Treatment of this alkene with concentrated sulphuric acid, however, led only to decomposition; the anticipated homoannular cyclisation to (3c) was not observed although analogous intramolecular alkylations have been reported.[9b,12]



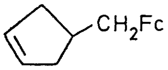
(10A)



(10B)

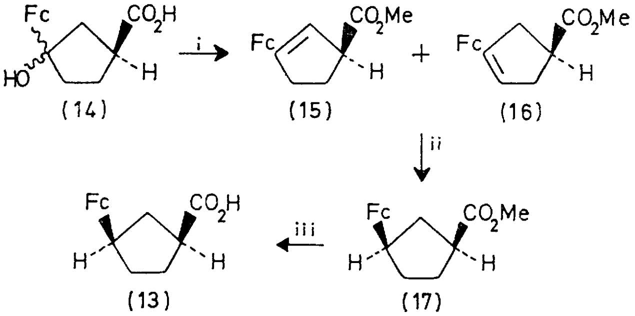


(11)



(12)

As an alternative approach, the synthesis of *cis*-3-ferrocenylcyclopentanecarboxylic acid (13) was required. The benzenoid analogue of this compound had been prepared[13] by Baker and Leeds by the reaction of benzene with cyclopent-1-enecarboxylic acid in the presence of aluminium chloride. However, when the same reaction was attempted using ferrocene as substrate, the required acid was not obtained. This compound was finally obtained by the sequence of reactions shown in the Scheme. Addition of ferrocenyl-lithium to 3-oxocyclopentanecarboxylic acid gave the hydroxy-acid (14) which was not characterised but was converted into a mixture of isomeric unsaturated esters (15) and (16) on treatment with acidified methanol. Catalytic hydrogenation of this mixture gave a single saturated ester (17). The *cis*-relationship of the ring substituents in this compound arises from the preferred direction of approach of the hydrogenation catalyst surface to the less-hindered side of the double bond in the cyclopentene precursors. The required acid (13) was obtained by hydrolysis of the saturated ester.



SCHEME Reagents: i, $MeOH/H_2SO_4$; ii, H_2–PtO_2; iii, NaOH then H_3O^+

In trifluoroacetic anhydride, the acid (13) underwent intramolecular cyclisation to give a mixture of two cyclic ketones (in the ratio 10 : 1) which were clearly the stereoisomers of the compound (4). The minor component of this mixture was identical with that which had previously been obtained by oxidation of (3c). Mixed-hydride reduction of these ketones afforded the corresponding derivatives (10A and B). The properties of the compound obtained from the major ketone product were quite distinct from those of its isomer which was identical with the compound (3c) previously obtained. In order to fully establish the stereoisomeric relationship of (10A and B), the pure compound obtained by hydrogenation of the addition product (2c) was treated with lithium in ethylamine, generating the cyclopentadienyl anions by metal–ligand fission.[14] Addition of ferrous chloride to this mixture gave a mixture of both (10A and B) which could be separated by g.l.c. By these experiments it was established that compound (3c), obtained by hydrogenation of the cyclopentadiene addition product (2c), represented a single stereoisomer which was identical with the product of reduction of the minor ketone from the cyclisation reaction.

It only remained to assign the structures (10A and B) to the two ferrocene derivatives which had been prepared. In a previous study,[10] we had mapped the shielding and deshielding regions around the ferrocene molecule. Inspection of Dreiding stereomodels of the

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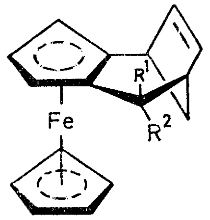
[11] E. A. Hill, *J. Org. Chem.*, 1963, **28**, 3586.

[12] S. G. Cottis and H. Rosenberg, *Chem. and Ind.*, 1963, 860; *cf.* E. W. Neuse, R. K. Crossland, and K. Koda, *J. Org. Chem.*, 1966, **31**, 2409; E. W. Neuse and R. M. Trahe, *J. Macromol. Chem.*, 1966, **1**, 611.

[13] W. Baker and W. G. Leeds, *J. Chem. Soc.*, 1948, 974.

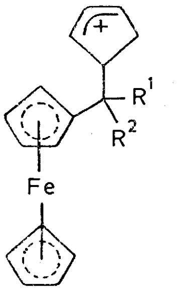
[14] *Cf.* J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 1961, 4604.

rigid molecular frameworks of these stereoisomers showed that five alkyl protons of the compound (10A) would be held in a shielding zone with two alkyl protons in a deshielding zone. For the stereoisomer (10B), the situation is reversed with five deshielded and two shielded alkyl protons expected. The structures of the compounds could thus be readily assigned from their ^1H n.m.r. spectra [(10A), τ 7·2—7·4 (2H) and 8·0—8·6 (5H); (10B) τ 7·3—7·6 (5H) and 8·45—8·8 (2H)] and it thereby followed that the cyclopentadiene addition product (2c) possessed the structure (18d). A crystal structure determination [15] of the product (2a), obtained by addition of cyclopentadiene to the cation (1a), revealed a similar stereochemistry with the bridging methylene group adjacent to the iron atom (18a).

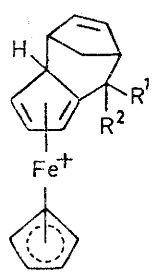


(18)

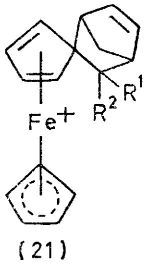
a; $R^1 = R^2 = $ Me
b; $R^1 = $ Me; $R^2 = $ H
c; $R^2 = $ Me; $R^1 = $ H
d; $R^1 = R^2 = $ H



(19)

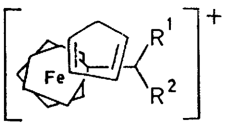


(20)



(21)

Various mechanisms can be written to account for the formation of the adducts (2) in the cyclopentadiene addition reactions. For example, electrophilic addition of the cations (1) to the diene would produce cyclopentenyl cations (19) which could lead to the observed products by internal electrophilic alkylation to give intermediates of the type (20), followed by proton elimination. However, the failure to observe acid-promoted cyclisation of 4-(ferrocenylmethyl)cyclopentene (*vide supra*) and the formation of adducts of a particular stereochemistry (18) [*cf.* cyclisation of (13)] casts doubts upon this pathway. Similarly, if the first step in the process involved the formation of spirocyclic intermediates (21), it seems unlikely that subsequent sigmatropic rearrangement to the intermediates (20) would proceed with the required stereoselectivity.



FIGURE

Consequently, we favour a mechanism in which the diene adds to the fulvene ligand of the cations (1) in a concerted fashion, formally a [6*s* + 4*s*] cycloaddition, to give the intermediates (20) directly, followed by proton loss. In this case, the molecular geometry of the products (18) requires that the reactants approach the transition state for cycloaddition with the relative orientation depicted in the Figure. Such an arrangement may be stabilised by secondary orbital interactions [16] between the reacting π systems and correspondingly favoured over the alternative orientation of approach.

In the reaction of the secondary cation (1b), two different adducts (18b and c) can result in principle depending upon the location of the methyl group with respect to the diene in the transition state for cycloaddition. Approach of the diene from the less-hindered direction (Figure; $R^1 = $ H, $R^2 = $ Me) would lead to the formation of a product containing an *exo*-methyl group [*i.e.* (18b)] while the alternative arrangement (Figure; $R^1 = $ Me, $R^2 = $ H) would produce the *endo*-methyl isomer (18c). In fact, two methyl doublets [τ 9·05 (*exo*-Me) and 8·55 (*endo*-Me); *cf.* ref. 10] were present in the ^1H n.m.r. spectrum of the product (2b) and their relative intensities were sensibly in accord with a product ratio (18b) : (18c) of *ca.* 10 : 1.

We have also investigated reactions of the cation (1a) with a range of 2π electron addends. In experiments [17] with cyclopentene, cyclohexene, *cis*- and *trans*-stilbene, ethyl propiolate, ethyl phenylpropiolate, and dimethyl acetylenedicarboxylate, however, we were unable to detect any products of cycloaddition. A similar lack of success attended efforts to effect cycloadditions between the cation (1a) and cycloheptatriene or furan.

EXPERIMENTAL

For general details, see Part IV.[18] Molecular weights were determined by accurate mass measurement of the molecular ions in the high resolution mass spectra.

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[15] T. S. Cameron, J. F. Maguire, T. D. Turbitt, and W. E. Watts, *J. Organometallic Chem.*, 1973, **49**, C79.

[16] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

[17] T. S. Abram, B.Sc. Thesis, New University of Ulster, 1973.

[18] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

Cyclopentadiene Addition Reactions.—(a) *With cation* (1a). A solution of triphenylmethyl tetrafluoroborate (3·3 g, 0·01 mol) in CH_2Cl_2 (20 ml) was added with stirring to a solution of 2-ferrocenylpropan-2-ol[19] (2·4 g, 0·01 mol) in CH_2Cl_2 (50 ml). The resulting brown solution of the cation (1a) was cooled to $-78°$ and an excess of freshly distilled cyclopentadiene (*ca*. 2 g) in CH_2Cl_2 (10 ml) was added dropwise. The mixture was stirred for 1 h at $-78°$ and then poured directly into water (200 ml). The organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in light petroleum and chromatographed. The following compounds were obtained in order of elution. Light petroleum eluted (*π-cyclopentadienyl*)[*η*-1—3a(8a)-4,7-*methano*-8,8-*dimethyl*-7,8-*dihydro*-4H-*azulenyl*]*iron*(II) (2a) (0·36 g, 12%), a yellow-orange solid, m.p. 100—101° (Found: C, 73·9; H, 6·9%; *M*, 292·0914. $C_{18}H_{20}Fe$ requires C, 74·0; H, 6·9%; *M*, 292·0894), τ 3·80 and 4·30 (1H and 1H, 2 × dd, vinyl), 5·85 (5H, s, π-C_5H_5), 6·05 (3H, m, C_5H_3), 6·9—8·0 (4H, m, $CHCH_2CH$), and 8·40 and 9·10 (3H and 3H, 2 × s, Me). The same solvent eluted 2-ferrocenylpropene (5) (0·11 g, 5%), a dark yellow solid, m.p. 76—77° (lit.,[20] 77·5—78·5°). The same solvent eluted a mixture of the 1,2-trimethyleneferrocene (8), m.p. 183—185° (lit.,[9] 186°) and the 1,1′-trimethyleneferrocene (9), m.p. 114—116° (lit.,[9] 116·5°); total yield (0·23 g, 8%). These isomers were separated by preparative t.l.c. The same solvent eluted a mixture of the isomeric diferrocenylpentenes (6) and (7), total yield (1·38 g, 50%), which were separated by preparative t.l.c. and whose properties agreed with those previously reported.[9] Finally, light petroleum–ether (3 : 1) eluted unchanged starting alcohol (0·12 g, 5% recovery).

When this reaction was repeated in the absence of cyclopentadiene, compounds (5)—(9) were obtained in approximately similar proportions.

(b) *With cation* (1b). A solution of cation (1b) in CH_2Cl_2 (70 ml) was generated from 1-ferrocenylethanol[21] (2·3 g, 0·01 mol) and triphenylmethyl tetrafluoroborate (3·3 g, 0·01 mol). Treatment of this solution with cyclopentadiene and work-up of the reaction as under (a) gave a product which was chromatographed. Light petroleum eluted the *adduct* (2b) (0·27 g, 10%), a yellow liquid (Found: C, 73·4; H, 6·4%; *M*, 278·0743. $C_{17}H_{18}Fe$ requires C, 73·4; H, 6·5%; *M*, 278·0757); τ 3·77 and 4·53 (1H and 1H, 2 × dd, vinyl), 5·97 (5H, s, π-C_5H_5), 6·02 (3H, m, C_5H_3), 6·5—7·9 (5H, m, $CHCH_2CHCH$), and 9·05 (3H, d, Me). This spectrum also contained a singlet at τ 5·87 (π-C_5H_5) and a doublet at 8·55 (Me), their intensities one-tenth of those of the corresponding resonances of the major constituent. A number of other compounds eluted on chromatography were oligomeric and were not characterised.

(c) *With cation* (1c). A solution of cyclopentadiene (3 ml) in CH_2Cl_2 (10 ml) was added dropwise to a stirred solution of chloromethylferrocene[11] (2·35 g, 0·01 mol) in CH_2Cl_2 (50 ml) at $-78°$. The mixture was stirred at $-78°$ for 2 h and then poured into water (200 ml). The organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was chromatographed. Light petroleum eluted the *adduct* (2c) (0·38 g, 14%), an orange-yellow liquid (Found: C, 72·7; H, 6·0%; *M*, 264·0599. $C_{16}H_{16}Fe$ requires C, 72·8; H, 6·1%; *M*, 264·0601), τ 3·85 and 4·40 (1H and 1H, 2 × dd, vinyl), 5·95 (5H, s, π-C_5H_5), 6·10 (3H, m, C_5H_3), and 6·8—8·1 (6H, m, alkyl). Light petroleum–ether (20 : 1) eluted bis(ferrocenylmethyl) ether (0·42 g, 20%) and light petroleum–ether (3 : 1) eluted ferrocenylmethanol (0·21 g, 10%), both identical with authentic samples.

Treatment of ferrocenylmethanol with triphenylmethyl tetrafluoroborate, followed by cyclopentadiene, as described under (a) gave bis(ferrocenylmethyl) ether as the sole product.

Attempted Reactions with Other Addends.—Treatment of cation (1a), generated in CH_2Cl_2 as described above, in turn with cyclohexa-1,3-diene, furan, cyclopentene, cyclohexene, cycloheptatriene, *cis*- and *trans*-stilbene, ethyl propiolate, ethyl phenylpropiolate, and dimethyl acetylenedicarboxylate did not afford products of cycloaddition. Only products derived from the cation (1a) itself [*i.e.* (5)—(9)] were isolated from these reactions.

Hydrogenation of Adducts (2).—Each of the adducts (2a and c) in ethanol was hydrogenated over PtO_2 catalyst, affording the corresponding saturated compounds (3a and c) in quantitative yields. *Compound* (3a) was obtained as a yellow solid, m.p. 67—68° (Found: C, 73·6; H, 7·5. $C_{18}H_{22}Fe$ requires C, 73·5; H, 7·5%), τ 5·86 (5H, s, π-C_5H_5), 6·07 (3H, m, C_5H_3), 7·2—7·5 and 7·5—8·5 (2H and 6H, 2 × m, alkyl), and 8·50 and 9·00 (3H and 3H, 2 × s, Me). *Compound* (3c) was obtained as a yellow liquid (Found: C, 72·3; H, 6·7. $C_{16}H_{18}Fe$ requires C, 72·2; H, 6·8%), τ 5·94 (5H, s, π-C_5H_5), 6·07 (3H, m, C_5H_3), and 7·2—7·4, 7·4—7·6, and 8·0—8·6 (2H, 3H, and 5H, 3 × m, alkyl). This compound gave a single peak on g.l.c. (SE 30 column at 210°).

Oxidation of Compound (3c).—A solution of (3c) (0·133 g, 0·5 mmol) in benzene (50 ml) was refluxed with 'active' manganese dioxide[22] (1 g) for 24 h. The mixture was filtered, the filtrate was evaporated, and the residue was chromatographed. Light petroleum eluted unchanged starting material (0·065 g, 50% recovery). Light petroleum–ether (3 : 1) eluted the *ketone* (4) (*isomer A*), an orange liquid (Found: C, 68·6; H, 5·7. $C_{16}H_{16}FeO$ requires C, 68·6; H, 5·7%), τ 5·20 and 5·50 (1H and 2H, 2 × m, C_5H_3), 5·74 (5H, s, π-C_5H_5), and 6·7—7·4 and 7·9—8·7 (3H and 5H, 2 × m, alkyl).

4-*Ferrocenoylcyclopentene* (11).—A solution of cyclopent-3-enecarbonyl chloride (1·1 g, 0·01 mol) in CH_2Cl_2 (10 ml) was added dropwise to a stirred solution of ferrocene (1·86 g, 0·01 mol) in CH_2Cl_2 (30 ml) containing aluminium chloride (1·3 g, 0·01 mol) at 0°. The mixture was stirred and allowed to reach room temperature during 4 h, and then was poured into water. The organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was chromatographed. Light petroleum eluted unchanged ferrocene (0·75 g, 40% recovery). Light petroleum–ether (3 : 1) eluted the *ketone* (11) (1·4 g, 50%), an orange-red compound, m.p. 77—78° (Found: C, 68·5; H, 5·7. $C_{16}H_{16}FeO$ requires C, 68·6; H, 5·7%); τ 4·31br (2H, s, vinyl), 5·29 and 5·50 (4H, 2 × t, C_5H_4), 5·80 (5H, s, π-C_5H_5), and 7·1—7·5 (5H, m, alkyl).

4-*Ferrocenylmethylcyclopentene* (12).—A solution of the ketone (11) (0·14 g, 0·5 mmol) in ether (20 ml) was added to a stirred suspension of lithium aluminium hydride (0·06 g, 1·5 mmol) and aluminium chloride (0·40 g, 3 mmol) in ether (20 ml). After 0·5 h, the excess of reagent was destroyed

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(EtOH) and the mixture was poured into water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was chromatographed. Light petroleum eluted the *alkene* (12) (0·12 g, 90%), a yellow liquid (Found: C, 72·4; H, 6·9. $C_{16}H_{18}Fe$ requires C, 72·2; H, 6·8%), τ 4·30br (2H, s, vinyl), 5·90 (5H, s, π-C_5H_5), 5·95 (4H, m, C_5H_4), and 7·4—7·9 (7H, m, alkyl). Treatment of this alkene with concentrated H_2SO_4 at 0° for 2 h caused extensive decomposition. No trace of the compound (3c) was detected.

Methyl 3-*Ferrocenylcyclopent*-2- *and* -3-*enecarboxylates* (15) *and* (16).—Butyl-lithium (2M in hexane; 11 ml) was added to a solution of ferrocene (3·7 g, 0·02 mol) in tetrahydrofuran (30 ml) and the mixture was stirred for 6 h at room temperature. A solution of 3-oxocyclopentanecarboxylic acid (1·1 g, 0·01 mol) in tetrahydrofuran (5 ml) was then added and the mixture was stirred for a further 1 h. The mixture was poured into water and extracted with ether. The extract was washed (H_2O) and then extracted with aqueous NaOH (10%, 50 ml). The basic extract was washed (Et_2O) and neutralised with aqueous HCl. The liberated acid was extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated, affording the crude hydroxy-acid (14). This acid was dissolved in methanol (50 ml) containing concentrated H_2SO_4 (1 ml), the solution was refluxed for 1 h, then diluted with water (200 ml), and extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was chromatographed. Light petroleum–ether (3 : 1) eluted a single orange-yellow band which afforded a 1 : 1 mixture (^1H n.m.r.) of the esters (15) and (16) (0·31 g, 10%) which was obtained as an orange oil (Found: C, 65·7; H, 5·8. Calc. for $C_{17}H_{18}FeO_2$: C, 65·8; H, 5·9%), τ 4·35 (1H, m, vinyl), 5·69 and 5·80 (4H, 2 × m, C_5H_4), 5·91 (5H, s, π-C_5H_5), 6·28 and 6·31 (3H, 2 × s, Me), and 7·0—8·5 (5H, m, alkyl).

Methyl cis-3-*Ferrocenylcyclopentanecarboxylate* (17).—A solution of the ester mixture (0·30 g, 1·0 mmol), from the previous experiment, in ethanol (20 ml) was stirred under H_2 in the presence of PtO_2 (50 mg). When uptake of H_2 had ceased, the solution was filtered, diluted with water, and extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was chromatographed. Light petroleum–ether (3 : 1) eluted a single band which afforded the *ester* (17) (0·30 g, 96%), a yellow liquid (Found: C, 65·5; H, 6·4. $C_{17}H_{20}FeO_2$ requires C, 65·4; H, 6·5%), τ 5·83 (5H, s, π-C_5H_5), 5·90 (4H, m, C_5H_4), 6·28 (3H, s, Me), and 7·0—8·3 (8H, m, alkyl).

cis-3-*Ferrocenylcyclopentanecarboxylic Acid* (13).—A solution of the ester (17) (0·29 g, 1·0 mmol) in ethanol (50 ml) containing aqueous NaOH (2M; 10 ml) was refluxed for 3 h. The solution was then diluted with water, neutralised (aqueous HCl), and extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated, giving the acid (13) (0·21 g, 75%) as a yellow liquid. This compound was used without further purification.

Attempted preparation of the acid (13) by the reaction of ferrocene with cyclopent-1-enecarboxylic acid and aluminium chloride in a range of solvents was unsuccessful.

Cyclisation of the Acid (13).—A solution of the acid (13) (0·15 g, 0·5 mmol) in trifluoroacetic anhydride (3 ml) and CCl_4 (2 ml) at 0° was stirred and allowed to reach room temperature over 6 h. The solution was then poured into water and extracted with ether. The extract was washed (H_2O), dried (K_2CO_3), and evaporated, and the residue was chromatographed. Light petroleum–ether (3 : 1) eluted a single orange band which afforded a mixture of the stereoisomeric forms of the ketone (4) (0·10 g, 73%) in the isomer ratio A : B 1 : 10 (see next experiment). The mixture was obtained as an orange liquid, τ 5·12, 5·45, and 5·56 (3H, 3 × m, C_5H_3), 5·75 (5H, s, π-C_5H_5), and 6·9—7·2, 7·6—7·9, and 8·2—8·4 (2H, 4H, and 2H, 3 × m, alkyl).

Reduction of Ketone (4).—A solution of the ketone mixture (0·10 g, 0·4 mmol), from the preceding experiment, in ether (10 ml) was added to a stirred mixture of lithium aluminium hydride (0·06 g, 1·5 mmol) and aluminium chloride (0·40 g, 3·0 mmol) in ether (20 ml). The mixture was stirred for 0·5 h and then poured carefully into water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was chromatographed. Light petroleum eluted a single yellow band which afforded compound (3c) (0·10 g. 100%). G.l.c. (SE30 column) showed that this sample comprised a mixture of the stereoisomers (10A) and (10B) in the ratio 1 : 10 respectively. The retention time of the minor constituent (10A) was identical with that of the compound (3c) obtained previously by hydrogenation of (2c.

Isomerisation of (10A).—The pure (g.l.c.) compound (10A) [from hydrogenation of (2c)] (27 mg, 0·01 mmol) was dissolved in ethylamine (7 ml). Lithium chips (*ca.* 100 mg) were added to this solution with stirring, and the mixture was stirred for 1 h. A solution of freshly prepared iron(II) chloride (200 mg) in tetrahydrofuran (10 ml) was then added and the mixture was stirred overnight. The mixture was poured into water and the resulting solution was extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was examined by g.l.c. This product contained a mixture of the stereoisomers (10A) and (10B) in the ratio 5 : 1 respectively.

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