Organoiron Complexes in Organic Synthesis. Part 7.[1] Regio- and Stereo-chemistry of Ring Connection Reactions relevant to Steroid and Terpene Synthesis. *X*-Ray Crystal Structure Determination of Tricarbonyl(methyl 1-[2—5-η-4-methoxy-1-methylcyclohexa-2,4-dienyl]-3-hydroxymethyl-3-methyl-2-oxocyclohexanecarboxylate)iron

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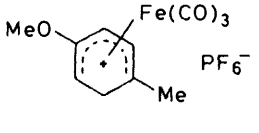
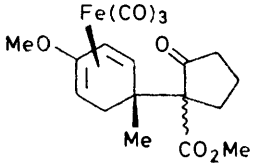
Reaction of tricarbonyl(1—5-η-4-methoxy-1-methylcyclohexadienylium)iron hexafluorophosphate (1) with enolate anions of derivatives of methyl 2-oxocyclohexanecarboxylate and methyl 1-oxotetralin-2-carboxylate occurs with very high regioselectivity for the methylated dienylium terminus. The structure and stereochemistry of one of the products (18) was determined by *X*-ray crystallography and found to be in agreement with that derived from spectroscopic data.

We recently described [2] the remarkable reaction between tricarbonyl(4-methoxy-1-methylcyclohexa-2,4-dienylium)iron hexafluorophosphate (1) and the potassium enolate of methyl 2-oxocyclopentanecarboxylate, which afforded in quantitative yield the two diastereoisomers (2) and (3). The application of this to the synthesis of trichothecanes is now being actively pursued in this laboratory. A useful extension of the reaction is to make an analogous connection between (1) and a cyclohexanone enolate, which might lead to compounds of use as intermediates in steroid or terpenoid total synthesis. The present paper describes our initial experiments in this area, together with results of the stereochemical course of the reaction when a *gem*-disubstituted keto-ester (11) is employed.



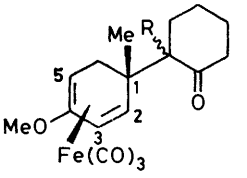
(1)



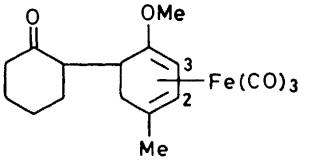
(2) α-CO_2Me (3) β-CO_2Me

RESULTS AND DISCUSSION

Reaction of (1) with the sodium or potassium enolate of methyl 2-oxocyclohexanecarboxylate gave, as expected, a mixture of the diastereoisomers (4) and (5) in very high yield. These compounds were readily separated by fractional crystallisation, and their structures were assigned by comparison of their proton n.m.r. spectra with (2) and (3), which have been completely characterised by n.m.r. spectroscopy and *X*-ray crystallography.[2] Thus, the higher-melting isomer (5) showed a similar spectrum to the higher-melting isomer (3), in that the methyl singlet was at higher field (δ 1.14) compared to (4) (δ 1.19), and a distinctive doublet of doublets (one of 6-H_2) occurred at δ 2.55 [2.69 in (3)], the corresponding signal for (4) being at higher field, obscured by the methylene envelope. Any application to steroid or terpenoid synthesis, assuming the keto-ester group would be in ring C, requires a demethoxycarbonylation step. Consequently, we considered alternatives to the use of keto-ester enolate anions. In our experience, use of ketone enolates is unsatisfactory in this reaction, resulting either in *O*-alkylation, or deprotonation of the complex.[3] Consequently, we examined the reaction of



(4) R = α-CO_2Me
(5) R = β-CO_2Me
(6) R = H



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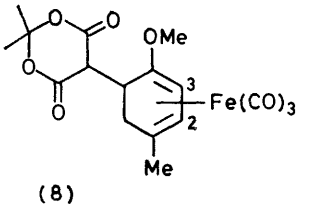

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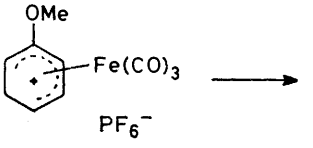

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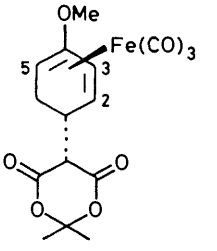
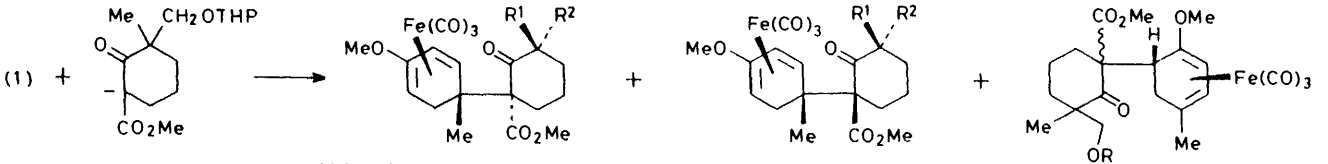


(10)

(1) with 1-morpholinocyclohexane in the hope that this could directly produce the complex (6). However, this reaction resulted entirely in formation of the alternative regioisomer (7) in low yield. Similarly, the enolate of Meldrum's acid attacked the unsubstituted terminus of (1) to give (8). That this behaviour is due largely to steric factors is shown by the fact that the enamine will

attack an unsubstituted dienylium terminus *para* to methoxy,[4] and our own observation that reaction between the non-methylated complex (9) and the enolate of Meldrum's acid gives exclusively the complex (10) (see Experimental section).

From the point of view of terpenoid synthesis we were interested in making a similar ring connection between the substituted keto-ester (11) and complexes related to (1). In this context we wished to assess whether the high regioselectivity observed above was maintained, and also whether the reaction is stereoselective on the

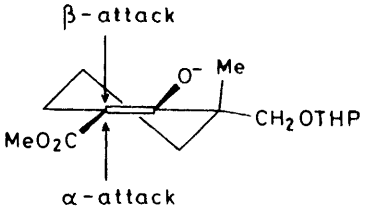


(12) R^1 = Me, R^2 = CH_2OTHP
(14) R^1 = CH_2OTHP, R^2 = Me
(17) R^1 = Me, R^2 = CH_2OH
(19) R^1 = CH_2OH, R^2 = Me

(13) R^1 = CH_2OTHP, R^2 = Me
(15) R^1 = Me, R^2 = CH_2OTHP
(18) R^1 = CH_2OH, R^2 = Me
(20) R^1 = Me, R^2 = CH_2OH

(16) R = THP
(21) R = H

enolate. We hoped that the large protected primary alcohol moiety would adopt a *quasi*-equatorial position in a chair conformation of the keto-ester enolate, when addition of cation would occur preferentially *trans* to the axial methyl group (α-attack), since the electrophile used is very bulky and would lead to a strong 1,3-diaxial interaction during β-attack (Scheme 1).[5]

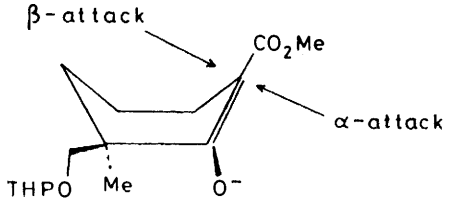


SCHEME 1

Reaction between (1) and the sodium enolate of (11) gave a mixture of products (n.m.r.). Chromatography on alumina gave a minor amount (15%) of a mixture of stereoisomers (16), followed by the mixture of stereoisomers (12)—(15) (85%). Use of the potassium enolate of (11) resulted in slightly lower overall yield. Thus, the reaction is still highly regioselective for the methylated terminus of (1). Further separation of the tetrahydropyranyl ethers was not possible, and the n.m.r. spectra were complicated by the presence of diastereoisomers from the protecting group. Hydrolysis of the major fraction to the corresponding alcohols gave a mixture which was partially separable by preparative t.l.c. (multiple development) to give a major band consisting of the diastereoisomers (17) and (18) and a minor band of (19) and (20) (ratio 1 : 6 : 1). Fractional crystallisation of each band allowed isolation of pure (18) and enriched samples (*ca.* 90% pure) of the other isomers. We were now in a position to assign tentative structures to these compounds, by comparison of n.m.r. spectra with the other similar diastereoisomeric pairs. As an example, (18) and (20) showed almost identical positions in the n.m.r. spectrum for 6-H and 2-H, to those given by (3) and (5), thus confirming the stereochemical relationship between the diene–$Fe(CO)_3$ and keto-ester groups. It remained to establish the relationship between primary alcohol and ester groups. We were unable to lactonise any of the isomers under the usual conditions [6] (benzene, toluene-*p*-sulphonic acid, reflux), and more forcing conditions led to considerable decomposition of the complex. The infrared spectra proved most informative, since the ketone absorption for (17) and (18) occurred at 1 700 cm^{-1}, whilst that for (19) and (20) was at 1 693 cm^{-1}. On the other hand, the ester absorption for (17) and (18) was at 1 720 cm^{-1}, the corresponding peak for (19) and (20) being at 1 727 cm^{-1}. This can be explained if the cyclohexanone ring adopts a chair conformation, with the diene–$Fe(CO)_3$ group equatorial. Thus, the CH_2OH group in (17) and (18), now axial, will hydrogen-bond to the ester but not the ketone, whilst in (19) and (20) this group is now equatorial and hydrogen-bonds to ketone and not ester. Acetylation of (19) and (20) resulted in a shift of the ketone absorption to 1 708 cm^{-1}, in agreement with this argument. Were the cyclohexanone ring to adopt a boat conformation with the diene–$Fe(CO)_3$ group equatorial, the stereochemical assignments based on these effects would be exactly the same. In order to confirm the stereochemical assignment, and also that the n.m.r. spectra could be interpreted as for (2) and (3) we undertook an *X*-ray crystallographic analysis of (18) (see later). From this study we can see that, although the regioselectivity of the reaction is still remarkably high, the reaction does not proceed with sufficient stereoselectivity on a monocyclic keto-ester to make it a synthetically attractive procedure. The most plausible explanation for this poor stereoselectivity is that the enolate anion can adopt chair or boat conformations, with the THP ether group equatorial. Both conformations then react with electrophile preferentially by α-attack, which is *trans* to the methyl group for the chair form (Scheme 1), and *cis* to the methyl group for the boat form (Scheme 2). Thus, the rapid reaction between (1) and the anion to a large extent reflects the equilibrium between chair and boat conformations.

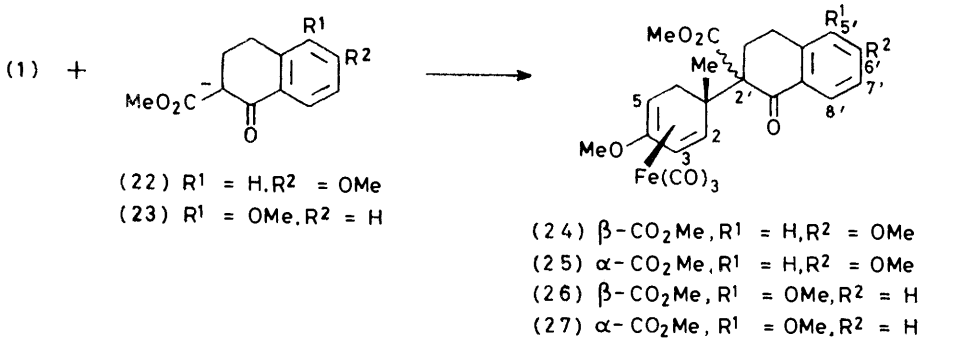
Treatment of the minor mixture of stereoisomeric THP ethers (16) in the above way allowed isolation of

one of the stereoisomers (21) as a pure crystalline compound. We were unable to assign the stereochemistry of this compound from spectroscopic data, and since these regioisomers were minor products this was pursued no further.



SCHEME 2

We next turned our attention to the reactions of (1) with the tetralone carboxylic ester enolates (22) and (23). Instantaneous reaction at 0 °C gave, in almost quantitative yield, the diastereoisomers (24) and (25) from (22), and (26) and (27) from (23). None of the products from attack at C-5 of (1) were observed, so again this reaction shows remarkable regiospecificity.



Each pair of diastereoisomers could be separated by fractional crystallisation, though only one isomer of each pair could be obtained pure in this case, the other crystallising in only 90% diastereoisomeric purity. We were unable to rigorously assign the stereochemistries of these products by n.m.r. spectroscopy, owing to overlaps in the methylene region, and the assignments given (see Experimental section) are based on comparison of the solubility with other members of the series we have now prepared.

This reaction is clearly of potential use in the synthesis of non-aromatic ring A steroids, provided the ring B fragment can be introduced, and we are currently examining the synthesis and reactivity of dienylium complexes which incorporate a lateral chain suitable for elaboration into this residue.

Description of Structure.—Molecules of (18) exist in the solid state as neutral, discrete monomers held together only by van der Waals forces. Figure 1 shows the molecular structure and includes the atom numbering scheme adopted. Tables 1 and 2 list the inter-bond lengths and angles, respectively.

As in other iron tricarbonyl complexes, the $Fe(CO)_3$ unit has approximate C_{3v} symmetry, with linear carbonyl groups. The metal is η^4-bound to C(2)—C(5) of the

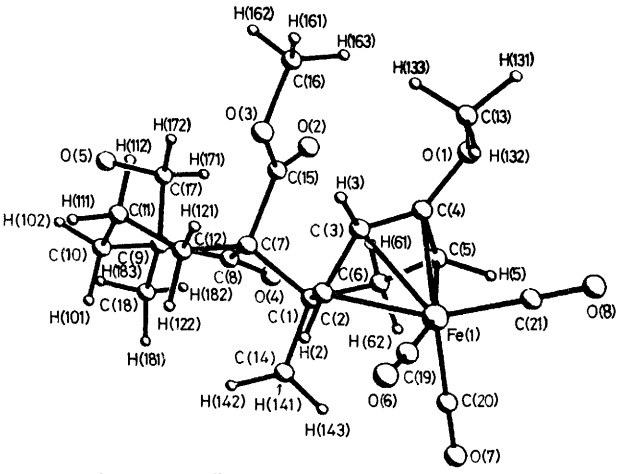


FIGURE 1 The molecular structure of (18)

cyclohexadiene ring. This unit is planar and makes an angle of 41.3° with the other fragment of the ring, an angle very similar to the value of 41.8° found in complex (3).[2] The methoxy-group is coplanar with the diene fragment of the ring. The carbon atom C(1) has an M-*endo*-methyl group and an M-*exo*-substituted cyclohexane ring bonded to it. The C(1)—C(7) distance is indicative of a single bond and should permit free rotation, although the energy barrier to this process might be sufficiently high to favour the conformation adopted in the crystal. The other axial site on C(7) is occupied by a methoxycarbonyl group, and the C(14)–C(1)–C(7)–C(15) torsion angle is −166.4° which shows an increase in

TABLE 1

Bond lengths (Å)

C(5)–Fe(1)	2.118(8)	C(6)–C(1)	1.521(12)
C(4)–Fe(1)	2.086(6)	C(2)–C(1)	1.536(10)
C(3)–Fe(1)	2.057(7)	C(7)–C(1)	1.613(11)
C(2)–Fe(1)	2.100(8)	C(14)–C(1)	1.541(11)
C(19)–Fe(1)	1.783(10)	C(5)–C(6)	1.482(11)
C(20)–Fe(1)	1.774(10)	C(4)–C(5)	1.422(10)
C(21)–Fe(1)	1.777(12)	C(3)–C(4)	1.418(12)
O(4)–C(8)	1.212(9)	O(1)–C(4)	1.364(9)
C(10)–C(9)	1.531(14)	C(2)–C(3)	1.428(10)
C(17)–C(9)	1.543(9)	C(8)–C(7)	1.546(11)
C(18)–C(9)	1.532(11)	C(12)–C(7)	1.518(10)
C(11)–C(10)	1.538(12)	C(15)–C(7)	1.556(10)
C(12)–C(11)	1.498(11)	C(9)–C(8)	1.545(16)
C(13)–O(1)	1.447(11)	O(2)–C(15)	1.204(9)
O(3)–C(15)	1.313(9)	C(16)–O(3)	1.459(10)
O(5)–C(17)	1.424(15)	O(6)–C(19)	1.161(11)
O(7)–C(20)	1.162(11)	O(8)–C(21)	1.147(12)

TABLE 2

Bond angles (°)

C(4)–Fe(1)–C(5)	39.5(3)	C(2)–C(1)–C(6)	107.5(7)
C(3)–Fe(1)–C(5)	69.9(3)	C(7)–C(1)–C(6)	114.5(6)
C(3)–Fe(1)–C(4)	40.0(3)	C(7)–C(1)–C(2)	107.4(6)
C(2)–Fe(1)–C(5)	75.0(3)	C(14)–C(1)–C(6)	111.5(7)
C(2)–Fe(1)–C(4)	68.9(3)	C(14)–C(1)–C(2)	109.4(6)
C(2)–Fe(1)–C(3)	40.2(3)	C(14)–C(1)–C(7)	106.4(7)
C(19)–Fe(1)–C(5)	162.4(4)	C(5)–C(6)–C(1)	112.9(6)
C(19)–Fe(1)–C(4)	126.4(4)	C(6)–C(5)–Fe(1)	109.5(5)
C(19)–Fe(1)–C(3)	92.7(4)	C(4)–C(5)–Fe(1)	69.0(4)
C(19)–Fe(1)–C(2)	90.1(4)	C(4)–C(5)–C(6)	120.4(7)
C(20)–Fe(1)–C(5)	93.0(4)	C(5)–C(4)–Fe(1)	71.5(4)
C(20)–Fe(1)–C(4)	132.4(4)	C(3)–C(4)–Fe(1)	68.9(4)
C(20)–Fe(1)–C(3)	140.0(4)	C(3)–C(4)–C(5)	114.9(7)
C(20)–Fe(1)–C(2)	101.4(4)	O(1)–C(4)–Fe(1)	126.0(6)
C(20)–Fe(1)–C(19)	99.1(4)	O(1)–C(4)–C(5)	119.0(8)
C(21)–Fe(1)–C(5)	95.5(4)	O(1)–C(4)–C(3)	126.0(7)
C(21)–Fe(1)–C(4)	90.8(4)	C(4)–C(3)–Fe(1)	71.1(4)
C(21)–Fe(1)–C(3)	117.8(4)	C(2)–C(3)–Fe(1)	71.5(4)
C(21)–Fe(1)–C(2)	157.7(4)	C(2)–C(3)–C(4)	112.6(6)
C(21)–Fe(1)–C(19)	95.2(6)	C(1)–C(2)–Fe(1)	112.9(6)
C(21)–Fe(1)–C(20)	99.1(5)	C(3)–C(2)–Fe(1)	68.3(4)
C(8)–C(7)–C(1)	109.0(6)	C(3)–C(2)–C(1)	120.2(7)
C(12)–C(7)–C(1)	112.7(6)	C(11)–C(10)–C(9)	113.7(8)
C(12)–C(7)–C(8)	111.7(6)	C(12)–C(11)–C(10)	109.0(7)
C(15)–C(7)–C(1)	109.1(6)	C(11)–C(12)–C(7)	115.4(6)
C(15)–C(7)–C(8)	103.3(6)	C(13)–O(1)–C(4)	116.0(7)
C(15)–C(7)–C(12)	110.5(6)	O(2)–C(15)–C(7)	125.6(7)
C(9)–C(8)–C(7)	121.2(7)	O(3)–C(15)–C(7)	112.7(7)
O(4)–C(8)–C(7)	122.0(7)	O(3)–C(15)–O(2)	121.7(7)
O(4)–C(8)–C(9)	116.6(7)	C(16)–O(3)–C(15)	116.1(7)
C(10)–C(9)–C(8)	113.2(7)	O(5)–C(17)–C(9)	110.7(8)
C(17)–C(9)–C(8)	106.1(8)	O(6)–C(19)–Fe(1)	177.1(9)
C(17)–C(9)–C(10)	109.4(7)	O(7)–C(20)–Fe(1)	178.0(9)
C(18)–C(9)–C(8)	109.4(8)	O(8)–C(21)–Fe(1)	176.6(10)
C(18)–C(9)–C(10)	109.1(9)	C(18)–C(9)–C(17)	109.6(6)

twist compared to the value of 177.0° found in (3).[2] The ester group shows the expected planarity at C(15). The cyclohexane ring adopts a distorted chair conformation with the ketonic carbon atom, C(8), exhibiting the expected planarity for sp^2 hybridisation. The methyl and hydroxymethyl substituents on this ring are respectively *trans* and *cis* to the methoxycarbonyl group.

EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 577, mass spectra with an A.E.I. MS30, and ^{1}H n.m.r. spectra with Varian EM360 (60 MHz) or HA100 (100 MHz) instruments. M.p.s were measured on a Kofler block. All chromatographic operations were conducted under nitrogen.

Tricarbonyl[methyl 1-(2—5-η-4-methoxy-1-methylcyclohexa-2,4-dienyl)-2-oxocyclohexanecarboxylate]iron Diastereoisomers (4) *and* (5).—To a stirred solution of potassium t-butoxide (0.7 g) in dry tetrahydrofuran (30 ml) under nitrogen was added dropwise methyl 2-oxocyclohexanecarboxylate (1.0 g) in tetrahydrofuran (10 ml). The resulting solution was stirred for 30 min and cooled to 0 °C. With back-flushing of nitrogen the flask was opened whilst tricarbonyl-(4-methoxy-1-methylcyclohexa-2,4-dienylium)iron hexafluorophosphate (1) (2.0 g) was added in portions. Complete reaction was evidenced by dissolution of the complex (*ca.* 15 min), whereupon most of the solvent was removed under reduced pressure at 30—40 °C. The product was extracted with ether in the usual way and washed with 10% aqueous hydrochloric acid, water, and sodium hydrogencarbonate solution to give a yellow solution which was dried ($MgSO_4$) and evaporated to give a yellow oil. Chromatography on silica gel with ether–light petroleum (b.p. 30—40 °C) (1 : 5 v/v) afforded an equimolar mixture of (4) and (5) (2.0 g, 97%). Recrystallisation from light petroleum (b.p. 30—40 °C) gave (5) as pale yellow *prisms*, m.p. 135—137 °C (from hexane); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 725sh, 1 710, and 1 488 cm^{-1}; δ($CDCl_3$) 4.98 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2.5 Hz, 3-H), 3.72 (3 H, s, CO_2Me), 3.59 (3 H, s, OMe), 3.23 (1 H, m, 5-H), 2.55 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, *exo*-6-H), 2.5—1.4 (10 H, 4 × CH_2, 2-H, *endo*-6-H), and 1.14 (3 H, s, Me); *m/e* 418 (40%), 390 (30), 334 (100), 302 (20), and 274 (75) (Found: C, 54.35; H, 5.25. $C_{19}H_{22}FeO_7$ requires C, 54.57; H 5.30%). Concentration of the mother-liquors gave the *complex* (4), m.p. 111—113 °C (from hexane); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 725sh, 1 710, and 1 488 cm^{-1}; δ($CDCl_3$) 5.08br (1 H, dd, 3-H), 3.76 (3 H, s, CO_2Me), 3.62 (3 H, s, OMe), 3.22 (1 H, m, 5-H), 2.36 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), 2.6—1.3 (10 H, m, 5 × CH_2), and 1.19 (3 H, s, Me); *m/e* 418 (5%), 390 (20), 334 (100), and 302 (35) (Found: C, 54.7; H, 5.2%).

Reaction of (1) *with* 1-*Morpholinocyclohexene*.—A suspension of (1) (0.50 g) in dry dichloromethane was stirred under nitrogen at room temperature with 1-morpholinocyclohexene [7] (0.30 ml) for 0.5 h. Acidification of the clear solution with aqueous 50% acetic acid (20 ml) containing sodium acetate (0.50 g), followed by extraction with ether and preparative t.l.c., afforded *tricarbonyl-(1—4-η-4-methoxy-1-methyl-5-(2-oxocyclohexyl)cyclohexadienyl]iron* (7) (0.10 g, 23%) as a mixture of pale yellow crystalline diastereoisomers, m.p. 81—95 °C; $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, and 1 705 cm^{-1}; δ($CDCl_3$) 5.18—5.32 (1 H, m, 3-H), 4.78—4.94 (1 H, m, 2-H), 3.38 and 3.36 (OMe, diastereoisomers), 1.49 (3 H, s, Me), and 2.60—1.02 (12 H, 5 × CH_2, 2 × CH); *m/e* 276 (*M* − 3CO) (Found: C, 56.5; H, 5.48. $C_{17}H_{20}FeO_5$ requires C, 56.69; H, 5.6%).

Reaction of (1) *with Meldrum's Acid*.—To a stirred suspension of sodium hydride (0.065 g; 50% dispersion in mineral oil, washed with dry pentane) in tetrahydrofuran (10 ml), at 0 °C under nitrogen, was added Meldrum's acid [8] (0.35 g) in tetrahydrofuran (10 ml). After stirring for 0.5 h the vessel was briefly opened with back-flushing of nitrogen whilst (1) (0.50 g) was added in one portion. Stirring was continued at 0 °C for 0.5 h, and at room temperature for 2 h, when the resulting yellow solution was poured into ether (50 ml) and washed successively with aqueous sodium hydrogencarbonate and water. The ether layer was dried ($MgSO_4$) and evaporated under vacuum and the resulting white solid was recrystallised from chloroform to give *tricarbonyl[1—4-η-5-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-4-methoxy-1-methylcyclohexa-1,3-dienyl]iron* (8) (0.36 g, 72%) m.p. 105—106 °C (decomp.); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 775, and 1 750 cm^{-1}; δ($CDCl_3$) 5.33 (1 H, d, *J* 4 Hz, 2-H), 4.95 (1 H, d, *J* 4 Hz, 3-H), 3.54—3.68 (2 H, m, 5-H and CO·OH·CO), 3.44 (3 H, s, OMe), 2.18 (1 H, dd, J_{gem} 15, $J_{5,6}$ 12 Hz, M-*endo*-6-H), 1.72 (6 H, s, CMe_2), 1.51 (3 H, s, Me), and 1.60—1.34 (1 H, m, M-*exo*-6-H); *m/e* 378 (*M* − CO; 5%), 350 (100), and 322 (90) (Found: C, 50,35; H, 4.4. $C_{17}H_{18}FeO_8$ requires C, 50.27; H, 4.47%).

Reaction of (9) *with Meldrum's Acid*.—Treatment of the hexafluorophosphate (9) [9] (0.50 g) with the sodio-derivative of Meldrum's acid (0.365 g) as above gave *tricarbonyl-[5-(2—5-η-4-methoxycyclohexa-2,5-dienyl)-2,2-dimethyl-1,3-dioxan-4,6-dione]iron* (10), recrystallised from chloroform (0.44 g, 97%), m.p. 140—141 °C (decomp.); $\nu_{max.}$ ($CHCl_3$) 2 060, 1 980, 1 780, 1 750, and 1 490 cm^{-1}; δ(CD_2Cl_2) 5.13 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 3 Hz, 3-H), 3.66 (3 H, s, OMe), 3.51 (1 H, d, *J* 4.5 Hz, CO·CH·CO), 3.30 (1 H, m, 5-H), 2.95 (1 H, m, 1-H),

2.59 (1 H, dd, $J_{2,3}$ 7, $J_{1,2}$ 3 Hz, 2-H), 2.19 (1 H, ddd, J_{gem} $J_{1,6}$ 10.5, $J_{5,6}$ 4 Hz, M-*endo*-6-H), 1.76 (6 H, s, CMe_2), 1.82 (1 H, m, M-*exo*-6-H); *m/e* 392 (*M*; 15%), 364 (20), 336 (100), and 308 (80) (Found: C, 48.9; H, 4.1. $C_{16}H_{16}FeO_8$ requires C, 49.01; H, 4.11%).

2-Hydroxymethyl-2-methylcyclohexanone.—To a stirred solution of potassium t-butoxide (2.1 g) in dry tetrahydrofuran (90 ml), under nitrogen, was added dropwise methyl 2-oxocyclohexanecarboxylate (3.0 g) in tetrahydrofuran (30 ml). The solution was stirred for 0.5 h, methyl iodide (5.45 g) was added, and the solution was stirred for 1 h at room temperature. An abundant precipitate of potassium iodide was formed. The mixture was poured into water and extracted with ether in the usual way, and the crude product was chromatographed on silica gel to give methyl 1-methyl-2-oxocyclohexanecarboxylate as a liquid (81%), $\nu_{max.}$ ($CHCl_3$) 1 725 and 1 705 cm^{-1}; δ($CDCl_3$) 3.77 (3 H, s, CO_2Me), 2.5 and 1.7 (8 H, m, 4 × CH_2), and 1.35 (3 H, s, Me). This compound (2.6 g) was dissolved in toluene (105 ml), and ethylene glycol (8.7 ml) and a catalytic amount of toluene-*p*-sulphonic acid were added. The mixture was refluxed with a water separator for 21 h, cooled and poured on to ice–water. The organic layer was separated, washed with 5% aqueous sodium carbonate and water, dried ($MgSO_4$), and evaporated to give the crude acetal (3.1 g) which was used without further purification, $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1}. This compound (2.9 g) was dissolved in tetrahydrofuran (140 ml), added to a stirred suspension of lithium aluminium hydride (1.2 g) in tetrahydrofuran (100 ml), and the stirred mixture was refluxed overnight. The usual work-up, followed by chromatography on silica gel gave 6-hydroxymethyl-6-methyl-1,4-dioxospiro[4.5]-decane as an oil eluted with 20% ether–benzene (1 : 5 v/v) (70%); $\nu_{max.}$ ($CHCl_3$) 3 500 cm^{-1}; δ($CDCl_3$) 4.0 (4 H, s, OCH_2CH_2O), 3.53br (2 H, s, CH_2OH), 2.96 (1 H, exch. D_2O, OH), 1.55 (8 H, 4 × CH_2), and 1.0 (3 H, s, Me); *m/e* 186 (8%), 170 (5), 169 (5), 155 (15), 124 (12), 123 (12), 113 (25), and 99 (100). Deprotection of the acetal (2.2 g) was achieved by treatment with hydrochloric acid (20 drops) in methanol (60 ml), dioxan (100 ml), and water (20 ml) at room temperature overnight. Extraction with ether followed by chromatography on silica gel gave pure *2-hydroxymethyl-2-methylcyclohexanone* as an oil (1.53 g, 91%); $\nu_{max.}$ ($CHCl_3$) 3 450 and 1 692 cm^{-1} (hydrogen-bonded ketone); δ($CDCl_3$) 3.54 (2 H, s, CH_2O), 2.8—1.4 (9 H, m, 4 × CH_2 and OH, exch. D_2O), and 1.22 (3 H, s, Me); M^+, 142 (Found: C, 67.45; H, 9.9. $C_8H_{14}O_2$ requires C, 67.51; H, 9.92%).

Methyl 3-Methyl-2-oxo-3-tetrahydropyranyloxymethylcyclohexanecarboxylate (11).—Dihydropyran (1.01 g) was added to 2-hydroxymethyl-2-methylcyclohexanone (0.70 g), followed by a catalytic amount of toluene-*p*-sulphonic acid, and the mixture was stirred for 1.5 h. Ice-cold aqueous sodium hydrogencarbonate was added and the product was extracted with ether. The extracts were washed with water and dried (Na_2CO_3), the solvent was evaporated, and the product was purified by chromatography on grade III basic alumina. Elution with 20% ether in hexane gave the pure tetrahydropyranyl ether (1.0 g, 81%); $\nu_{max.}$ ($CHCl_3$) 1 703, 1 120, and 1 030 cm^{-1}; δ($CDCl_3$) 4.53br (1 H, THP-ether CH), 3.9—3.4 (4 H, ABq + m, 2 × CH_2O), 2.6—1.5 (14 H, 7 × CH_2), and 1.10 and 1.07 (2 × CH_3 diastereoisomers). Sodium hydride (600 mg, dispersion in oil washed with pentane) was stirred in dry dioxan (5 ml) under nitrogen and dimethyl carbonate (2.8 g) was added. The temperature of the mixture was raised to 80—85 °C and the above tetrahydropyranyl ether (1.5 g) in tetrahydrofuran (5 ml) was added dropwise over 1 h. The dark orange mixture was stirred for a further 2.5 h at this temperature, cooled to 0 °C, and carefully treated with methanol, followed by a slight excess of acetic acid. The product was taken up in ether and the solution was washed with aqueous sodium hydrogencarbonate and saturated brine, dried ($MgSO_4$), and evaporated. Chromatography on grade III neutral alumina (45 g) gave the expected diastereoisomeric *keto-ester tetrahydropyranyl ethers* as an oil, eluted with 15% v/v ether–hexane (1.4 g, 74%), as a mixture of keto and enol forms; $\nu_{max.}$ ($CHCl_3$) 1 740, 1 710, 1 650, and 1 610 cm^{-1}; δ($CDCl_3$) 4.53br (1 H, THP-ether CH), 3.80 (3 H, s, CO_2Me), 4.1—3.4 (5 H, keto-ester CH, and 2 × CH_2O), 2.5—1.5 (12 H, m, 6 × CH_2), and 1.15 (3 H, s, Me); *m/e* 284 (15%), 254 (20), 200 (40), and 170 (100) (Found: C, 63.15; H 8.6. $C_{15}H_{24}O_5$ requires C, 63.36; H, 8.51%).

Reaction of Hexafluorophosphate (1) *with Methyl 3-Methyl-2-oxo-1-sodio-3-tetrahydropyranyloxymethylcyclohexanecarboxylate.*—Sodium hydride (0.168 g; 50% dispersion in mineral oil, washed with pentane) was stirred in tetrahydrofuran (10 ml) under nitrogen whilst the above keto-ester (0.77 g) in tetrahydrofuran (14 ml) was added dropwise. The resulting pale yellow solution was stirred for 0.5 h, after which time the vessel was opened briefly and, with back-flushing of nitrogen, the hexafluorophosphate (1) (1.26 g) was added. Stirring was continued for 0.5 h and the reaction worked up as previously. Chromatography on grade III basic alumina gave the mixture of stereoisomers (16) eluted with ether–hexane (1 : 9 v/v) (200 mg, 15% from protected keto-ester) showing an expectedly complex ^1H n.m.r. spectrum. The absence of regioisomers of structure (12)—(15) was indicated by the absence of the band at *ca.* 1 490 cm^{-1} characteristic of that substitution pattern. The presence of the regioisomer (16) is shown by the presence of the typical AB patterns (H-2, H-3) in the region δ 4.8—5.4, and the presence of the 4-methoxy-resonances at *ca.* δ 3.4 in the n.m.r. spectrum [regioisomers (12)—(15) show this group at *ca.* δ 3.6]. Further characterisation was carried out after hydrolysis of the THP-ether group (see later). Further elution afforded the mixture of complexes (12)—(15) (1.555 g, 85%) which could not be further separated and so complete characterisation of the mixture was carried out after deprotection of the alcohol group.

Isolation and Characterisation of Complexes (17)—(20).—The mixture of THP ethers (12)—(15) (0.70 g) was stirred, under nitrogen, in dioxan (20 ml), methanol (15 ml), and water (5 ml), and concentrated hydrochloric acid (20 drops) was added. After 2 h the mixture was poured onto ice–water and the product extracted with ether. The organic layer was washed to neutrality with water, dried ($MgSO_4$), and evaporated. The mixture was subjected to preparative t.l.c. on silica gel, developing twice with hexane–ethyl acetate–ether (5 : 3 : 2 v/v/v). Two bands separated, and these were extracted to give a mixture of (17) and (18) (0.29 g) and a mixture of (19) and (20) (0.18 g). The mixture of (17) and (18) was recrystallised from hexane–ether to give *tricarbonyl-[methyl 3-hydroxymethyl-1-(2—5-η-4-methoxy-1-methylcyclohexa-2,4-dienyl)-3-methyl-2-oxocyclohexane-1-carboxylate]iron* (18) which was obtained pure after a second recrystallisation as pale yellow needles, m.p. 138—139 °C (0.13 g); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 720sh, 1 700, and 1 488 cm^{-1}; δ($CDCl_3$) 5.0 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2 Hz, 3-H), 3.75 (3 H, s, CO_2Me), 3.60 (3 H, s, OMe), 3.40 (2 H,

AB q, CH_2OH), 3.27 (1 H, m, 5-H), 2.79 (1 H, dd, J_{gem} 16, $J_{5,6}$ 2 Hz, 6-H), 2.6br (1 H, OH), 2.41 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), 2.1—1.2 (7 H, m, 3 × CH_2 and 6-H), 1.10 (3 H, s, Me), and 1.08 (3 H, s, Me); *m/e* 434 (16%; *M* − CO), 378 (100; *M* − 3CO) (Found: C, 54.55; H, 6.0. $C_{21}H_{28}FeO_8$ requires C, 54.33; H, 6.08%). This compound was subjected to *X*-ray analysis. Concentration of the mother-liquors and crystallisation afforded (17) containing *ca.* 10% of (18) (0.12 g). This was not further purified. Compound (17) showed $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 720sh, 1 700, and 1 488 cm^{-1}; δ($CDCl_3$) 5.04br (1 H, 3-H), 3.77 (3 H, s, CO_2Me), 3.64 (3 H, s, OMe), 3.46 (2 H, m, CH_2OH), 3.20 (1 H, m, 5-H), 2.4 (2 H, m), and 2.0—1.2 (8 H, m) (2-H, OH and 4 × CH_2), and 1.12 (6 H, s, 2 × Me). The mixture of diastereoisomers (19) and (20) was subjected to multiple-development preparative t.l.c. on silica gel with hexane–ethyl acetate–ether (5 : 3 : 2 v/v/v) giving *ca.* 90% single isomer (19) (0.095 g) and *ca.* 90% single isomer (20) (0.08 g) as pale yellow gums. Further separation was not pursued. Compound (19) showed $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 727, 1 693, and 1 488 cm^{-1}; δ($CDCl_3$) 5.08br (1 H, 3-H), 3.74 (3 H, s, CO_2Me), 3.65 (3 H, s, OMe), 3.5 (2 H, m, CH_2OH), 3.23 (1 H, m, 5-H), 2.4 (3 H, m) and 1.8—1.0 (6 H, m) (2-H and 4 × CH_2), 1.20 (3 H, s, Me), and 1.04 (3 H, s, Me); *m/e* 434 (10%; *M* − CO), 378 (100; *M* − 3CO), 346 (60), and 318 (60) (Found: C, 54.2; H, 6.15. $C_{21}H_{28}FeO_8$ requires C, 54.33; H, 6.08%); compound (20) showed $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 727, 1 693, and 1 488 cm^{-1}; δ($CDCl_3$) 4.98 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2.5 Hz, 3-H), 3.71 (3 H, s, CO_2Me), 3.61 (3 H, s, OMe), 3.4 (2 H, m, CH_2OH), 3.16 (1 H, m, 5-H), 2.88br (1 H, dd, J_{gem} 16, $J_{5,6}$ *ca.* 2 Hz, 6-H), 2.36 (1 H, d, $J_{2,3}$ 6 Hz, 3-H), 2.4 and 1.9—1.2 (total 8 H, 3 × CH_2, 6-H, and OH), 1.10 (3 H, s, Me), and 0.98 (3 H, s, Me); *m/e* 434 (25%; *M* − CO), 378 (100) (*M* − 3CO), 346 (60), and 318 (60).

Tricarbonyl[methyl 3-hydroxymethyl-1-(2—5-η-2-methoxy-5-methylcyclohexa-2,4-dienyl)-3-methyl-2-oxocyclohexane-1-carboxylate]iron (21).—The mixture of stereoisomeric THP ethers (16) was treated as above, giving a crude hydrolysis product which showed one major spot on t.l.c. Recrystallisation from hexane–ether gave a single isomer of (21) as pale yellow needles, m.p. 112—116 °C (30 mg); $\nu_{max.}$ ($CHCl_3$) 2 045, 1 973, 1 727, and 1 700 cm^{-1}; δ ($CDCl_3$) 5.34 (1 H, d, $J_{3,4}$ 5 Hz, 3-H), 4.82 (1 H, d, $J_{3,4}$ 5 Hz, 4-H), 3.68 (3 H, s, CO_2Me), 3.43br (2 H, s, CH_2OH), 3.28 (3 H, s, OMe), 2.2—1.2 (10 H, 4 × CH_2, CH, OH), 1.49 (3 H, s, 5-Me), 1.14 (3 H, s, Me); *m/e* 434 (3%; *M* − CO), 406 (15; *M* − 2CO), and 378 (100; *M* − 3CO) (Found: C, 54.25; H, 6.3. $C_{21}H_{28}FeO_8$ requires C, 54.33; H, 6.08%).

Tricarbonyl[methyl 6-methoxy-2-(2—5-η-4-methoxy-1-methylcyclohexa-2,4-dienyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate]iron Diastereoisomers (24) *and* (25).—The sodio-derivative of methyl 6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (0.143 g) was prepared and treated as above with the hexafluorophosphate (1) (0.25 g) (reaction time 20 min, room temperature) to give the product as a 1 : 1 mixture of diastereoisomers (24) and (25) (0.289 g, 96%) free from regioisomeric or other impurity (n.m.r.). Recrystallisation from ether–pentane (1 : 1 v/v) afforded the pure *ester* (24), m.p. 121—123 °C (decomp.); $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, 1 720, 1 675, 1 600, and 1 490 cm^{-1}; δ ($CDCl_3$) 7.94 (H, d, *J* 8 Hz, 8′-H), 6.78 (1 H, dd, *J* 8 and 2 Hz, 7′-H), 6.59 (1 H, d, *J* 2 Hz, 5′-H), 5.05 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 2 Hz, 3-H), 3.82 (3 H, s, ArOMe), 3.60 (3 H, s, 4-OMe), 3.58 (3 H, s, CO_2Me), 3.29 (1 H, m, 5-H), 3.13—1.5 (7 H, several m, 2-H, 6-H_2, 3′-H_2, and 4′-H_2), and 1.22br (3 H, s, Me); *m/e* 356 [*M* − $Fe(CO)_3$] (Found: C, 58.0; H, 5.05. $C_{24}H_{24}FeO_8$ requires C, 58.08; H, 4.87%). Evaporation of the liquors gave (25) *ca.* 80% pure, δ ($CDCl_3$) 7.96 (1 H, d, *J* 8 Hz, 8′-H), 6.78 (1 H, dd, *J* 8 and 2 Hz, 7′-H), 6.59 (1 H, d, *J* 2 Hz, 5′-H), 5.05 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 2 Hz, 3-H), 3.82 (3 H, s, ArO*Me*), 3.62 (3 H, s, CO_2Me), 3.60 (3 H, s, 4-OMe), 3.29 (1 H, m, 5-H), 3.06—1.52 (7 H, several m, 2-H, 6-H_2, 3′-H_2, and 4′-H_2), and 1.32br (3 H, s, Me).

Tricarbonyl[methyl 5-methoxy-2-(2—5-η-4-methoxy-1-methylcyclohexa-2,4-dienyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate]iron Diastereoisomers (26) and (27).—Treatment of the sodio-derivative of methyl 5-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (0.53 g) with the hexafluorophosphate (1) (0.92 g) as above gave a 1 : 1 mixture of (26) and (27), homogeneous on t.l.c. (1.1 g, 98%). A single recrystallisation from 25% ether in pentane gave (26), 90% single isomer, as white *crystals*, m.p. 115—120 °C (decomp.); $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, 1 720, and 1 685 cm^{-1}; δ ($CDCl_3$) 7.60 (1 H, d, *J* 8 Hz, 8′-H), 7.23 (1 H, dd, *J* 8 and 8 Hz, 7′-H), 6.95 (1 H, d, *J* 8 Hz, 6′-H), 5.07 (1 H, m, 3-H), 3.83 (3 H, s, ArOMe), 3.62 (6 H, s, CO_2Me and 4-OMe), 3.23 (1 H, m, 5-H), 2.96—1.4 (7 H, several m, 2-H, 6-H_2, 3′-H_2, and 4′-H_2), and 1.32br (3 H, s, Me); *m/e* 356 [*M* − $Fe(CO)_3$] (Found: C, 58.3; H, 4.95. $C_{24}H_{24}FeO_8$ requires C, 58.08; H, 4.96%). Evaporation of the liquors gave (27), 80% single diastereoisomer; δ ($CDCl_3$) 7.58 (1 H, d, *J* 8 Hz, 8′-H) 7.23 (1 H, dd, *J* 8 and 8 Hz, 7′-H), 6.95 (1 H, d, *J* 8 Hz, 6′-H), 5.07 (1 H, m, 3-H), 3.83 (3 H, s, ArO*Me*), 3.62 (3 H, s, 4-OMe), 3.58 (3 H, s, CO_2Me), 3.29 (1 H, m, 5-H), 3.04—1.48 (7 H, 2-H, 6-H_2, 3′-H_2, and 4′-H_2), and 1.25 (3 H, s, br, Me).

X-*Ray Structural Analysis*.—Pale yellow needles of (18) were deposited from hexane–ether. The crystals were slightly air-sensitive and several were mounted in 0.5-mm Lindemann tubes under nitrogen. A suitable single crystal with dimensions *ca.* 0.33 × 0.25 × 0.22 mm was chosen for the analysis, and cell dimensions and space group determined from preliminary Weissenberg photographs. The crystal was mounted on a Nonuis CAD4 diffractometer. Accurate cell parameters were obtained from the angular measurement of 25 reflections in the range of $14 < \theta < 15°$. 1 643 Reflections were recorded to a $2\theta_{max.}$ of 44.0°, using graphite-monochromated Mo-K_α radiation and an $\omega/2\theta$ scan technique. The scan width was calculated according to the equation ' width = $A + B \tan\theta$ ' with $A = 0.80°$ and $B = 0.35°$. Each reflection was subjected to a 0.5-s prescan and if the measured count was < 3 counts s^{-1} it was not re-measured. Throughout the course of the data collection two reflections were re-measured at regular intervals but showed no significant variation in intensity. Lorentz and polarisation, but not absorption, corrections, were applied and equivalent reflections were averaged to give 1 139 unique observed $|F > 3\sigma(F)|$ intensities.

Crystal data. $C_{21}H_{28}FeO_8$, $M = 464.28$, $a = 28.059$ (11), $b = 7.793$ (3), $c = 9.914$ (4) Å, $U = 2\,167.8$ Å^3, $D_m = 1.42$, $Z = 4$, $D_c = 1.422$ g cm^{-3}, $F(000) = 975.96$, Mo-K_α radiation, $\lambda = 0.71\,069$ Å, μ(Mo-K_α) = 7.05 cm^{-1}, space group $Pca2_1$ from systematic absences and successful refinement.

The iron atom position was derived from a Patterson synthesis and the remaining non-hydrogen atoms were located from subsequent Fourier-difference maps. The structure was refined by full-matrix least-squares to an *R*

of 0.081 with all atoms assigned individual isotropic temperature factors. A difference electron-density map calculated at this stage revealed the positions of most of the hydrogen atoms. All the hydrogen atoms except for the hydroxy-H, which was not located, were placed in geometrically idealised positions and were constrained to ride 1.08 Å from the relevant carbon atoms. The >CH– and >CH_2-group hydrogen atoms were assigned a common isotropic thermal parameter as were the methyl hydrogen atoms; the methyl groups were refined as rigid bodies. Refinement continued with the iron and oxygen atoms assigned anisotropic thermal parameters. In the final cycles of refinement a weighting scheme of the form $w = 1.728\ 0/|\sigma^2(F) + 0.0004\ |F|^2|$ was introduced. This reduced the dependence of $\Delta\omega^2$ on $|F_o|$ and sin θ. The converged residuals were $R = 0.047$ and $R'[= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0.044$. A final difference electron density map showed no remaining regions of significant electron density.

Complex neutral-atom scattering factors were employed throughout.[10] Table 3 lists the final atomic parameters for non-hydrogen atoms and Table 4 the hydrogen atom parameters, while details of thermal parameters, molecular planes, angles involving hydrogen atoms, and observed and calculated structure-factor amplitudes may be found in Supplementary Publication No. SUP 22873 (11 pp.).* Computing was carried out on the University of Cambridge IBM 370/165 computer using 'SHELX 76,'[11] and the plotting program PLUTO written by Dr. W. D. S. Motherwell.

TABLE 3

Atom co-ordinates (× 10^4)

	x/a	*y/b*	*z/x*
Fe(1)	9 437(1)	4 899(2)	2 236(1)
C(1)	9 032(3)	2 447(9)	4 337(9)
C(6)	8 861(3)	1 849(10)	2 960(9)
C(5)	8 845(3)	3 252(10)	1 952(8)
C(4)	8 695(2)	4 926(9)	2 333(10)
C(3)	8 898(3)	5 551(9)	3 546(8)
C(2)	9 198(3)	4 317(9)	4 190(9)
C(7)	8 631(3)	2 405(9)	5 501(8)
C(8)	8 511(3)	516(11)	5 837(10)
C(9)	8 329(2)	−7(10)	7 249(14)
C(10)	8 492(3)	1 214(12)	8 368(10)
C(11)	8 470(3)	3 119(10)	7 969(10)
C(12)	8 776(3)	3 403(10)	6 751(8)
O(1)	8 397(2)	5 813(7)	1 497(6)
C(13)	8 390(4)	7 656(12)	1 675(11)
C(14)	9 449(3)	1 340(11)	4 851(10)
C(15)	8 155(3)	3 114(10)	4 919(9)
O(2)	7 872(2)	2 310(7)	4 258(8)
O(3)	8 084(2)	4 735(6)	5 222(6)
C(16)	7 657(3)	5 521(12)	4 654(12)
O(4)	8 521(2)	−603(7)	4 988(6)
C(17)	7 780(3)	13(11)	7 165(14)
O(5)	7 575(3)	−591(8)	8 391(9)
C(18)	8 501(3)	−1 826(11)	7 576(10)
C(19)	9 830(4)	6 480(12)	2 910(10)
O(6)	10 070(3)	7 538(11)	3 379(8)
C(20)	9 855(3)	3 227(12)	1 954(10)
O(7)	10 118(3)	2 107(11)	1 749(8)
C(21)	9 422(3)	5 790(14)	587(12)
O(8)	9 401(2)	6 292(11)	−500(7)

TABLE 4

Hydrogen atom co-ordinates (× 10^4) and isotropic temperature factors (Å² × 10^3)

	x/a	*y/b*	*z/c*	*U*
H(61)	8 506(3)	1 324(10)	3 065(9)	60(7)
H(62)	9 099(3)	864(10)	2 597(9)	60(7)
H(5)	8 951(3)	3 009(10)	922(8)	95(19)
H(3)	8 835(3)	6 824(9)	3 938(8)	95(19)
H(2)	9 542(3)	4 701(9)	4 576(9)	95(19)
H(101)	8 856(3)	905(12)	8 630(10)	60(7)
H(102)	8 266(3)	1 020(12)	9 235(10)	60(7)
H(111)	8 598(3)	3 898(10)	8 794(10)	60(7)
H(112)	8 106(3)	3 467(10)	7 739(10)	60(7)
H(121)	8 766(3)	4 753(10)	6 508(8)	60(7)
H(122)	9 135(3)	3 035(10)	7 007(8)	60(7)
H(131)	8 185(4)	8 112(12)	824(11)	72(8)
H(132)	8 732(4)	8 288(12)	1 688(11)	72(8)
H(133)	8 201(4)	7 939(12)	2 597(11)	72(8)
H(141)	9 344(3)	9(11)	4 782(10)	72(8)
H(142)	9 564(3)	1 618(11)	5 868(10)	72(8)
H(143)	9 739(3)	1 583(11)	4 160(10)	72(8)
H(161)	7 706(3)	6 896(12)	4 652(12)	72(8)
H(162)	7 377(3)	5 185(12)	5 352(12)	72(8)
H(163)	7 561(3)	5 098(12)	3 653(12)	72(8)
H(171)	7 667(3)	−799(11)	6 341(14)	60(7)
H(172)	7 659(3)	1 309(11)	6 988(14)	60(7)
H(181)	8 886(3)	−1 863(11)	7 589(10)	72(8)
H(182)	8 369(3)	−2 699(11)	6 817(10)	72(8)
H(183)	8 366(3)	−2 201(11)	8 552(10)	72(8)

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REFERENCES

[1] Part 6, A. J. Pearson and M. Chandler, *J.C.S. Perkin I*, 1980, 2238.
[2] A. J. Pearson and P. R. Raithby, *J.C.S. Perkin I*, 1980, 395.
[3] A. J. Pearson, unpublished observations.
[4] R. E. Ireland, G. G. Brown, jun., R. H. Stanford, jun., and T. C. McKenzie, *J. Org. Chem.*, 1974, **39**, 51.
[5] (*a*) H. O. House, 'Modern Synthetic Reactions,' W. A. Benjamin, 2nd edn., 1972; (*b*) D. Caine, in 'Carbon Carbon Bond Formation,' vol. 1, Techniques and Applications in Organic Synthesis, ed. R. L. Augustine, Marcel Dekker, 1979, p. 85, and references therein.
[6] R. E. Ireland, D. E. Evans, D. Glover, G. M. Rubottom, and H. Young, *J. Org. Chem.*, 1969, **34**, 3717.
[7] F. W. Heyl and M. E. Herr, *J. Amer. Chem. Soc.*, 1953, **75**, 1918.
[8] H. McNab, *Chem. Soc. Rev.*, 1978, **7**, 345.
[9] A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882.
[10] 'International Tables for *X*-ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
[11] G. M. Sheldrick, 'SHELX 76—A Crystallographic Computer Programming Package,' University of Cambridge, 1976.

* For details, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.