Organometallic Compounds in Organic Synthesis. Part 14.[1] Tricarbonyliron as Lateral Control Group in the Selective Alkaline Hydrolysis of some Cyclohexa-1,3-diene Carboxylic Esters

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Alkaline hydrolyses of a number of methoxycarbonyl derivatives of cyclohexa-1,3-diene–$Fe(CO)_3$ have been used as indices of steric and electronic effects on reactivities of the ester groups. A β-CO_2Me or a 1-CO_2Me group is resistant to hydrolysis for steric and electronic reasons, respectively. A number of substituted esters are examined and, with dicarboxylic esters complexation used successfully to enable half hydrolyses, which cannot readily be accomplished with the parent esters.

SELECTIVE reactivities of identical functional groups in the same molecule are frequently required for synthetic purposes. This selectivity is often obtained by reversible alterations of structure which achieve their purpose by steric or electronic effects. Classical alterations of ester hydrolyses, for example, are produced by alterations of the alkyl group. In multi-functional molecules the required alterations may lead to experimental difficulties and extension of the range of possibilities is desirable. In the work described herein with some cyclohexadienecarboxylates, we examined the reversible complexing of the acid portion, rather than change of the alkyl portion.

As it is a well understood process,[2] the alkaline hydrolysis of esters is a convenient vehicle to study both the steric and electronic effects of superimposed $Fe(CO)_3$. It is experimentally convenient in the separation of water-soluble salts and the synthetic capabilities of CO_2R and CO_2H are considerable. Selective reactions in multi-functional molecules, such as dicarboxylic esters are desirable, and hydrolyses form one basis for further elaborations of groups such as CO_2H or CO_2R.

RESULTS AND DISCUSSION

Monocarboxylic Esters.—The esters (1) (1-Co_2Me), (11) (2-CO_2Me), (15) (5α-CO_2Me), and (21) (5β-CO_2Me) were subjected to standard mild alkaline hydrolysis (Table 1). The products were identified by ^1H n.m.r. spectroscopy. The complex (1) was recovered, in accord with previous results,[3] while the esters (11) and (15) gave the corresponding carboxylic acids. The 5β-complex (21) gave rise not only to the corresponding acid, but to some 5α-CO_2H, corresponding to the ester (15), and also, by structural isomerisation, to the unhydrolyzed 1-CO_2Me isomer (1). The course of these transformations is discussed below.

The 1-CO_2Me cyclohexadiene complexes which contain either Me or OMe groups at the 2-, 3-, 4- or 6-positions (entries 5—19, Table 1), were also recovered, largely unchanged, from alkaline treatment. The inhibition of hydrolysis seems, therefore, to be a general one, which might be used for protective purposes.

The complexes (2) (2-Me, 1-CO_2Me) and (3) (6-Me, 1-CO_2Me) were produced as a mixture from 2-methylbenzoic acid by the sequence: Birch reduction of 2-

methylbenzoic acid,[4] methylation, and complexation with isomerization. Since the mixture could not be separated by standard physical methods, use was made of hydride abstraction by trityl cation, which is known to be
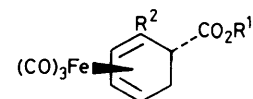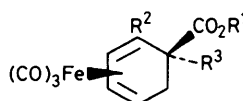
All R^n = H unless stated otherwise
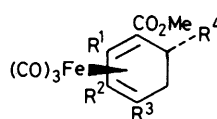
(1)

(2) R^1 = Me
(3) R^4 = Me
(4) R^2 = Me
(5) R^1 = OMe
(6) R^2 = OMe
(7) R^3 = OMe
(8) R^3 = CO_2Me
(9) R^3 = CO_2H
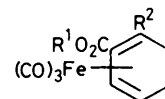
(10)

(11) R^1 = Me
(12) R^1 = Me, R^2 = OMe
(13) R^2 = OMe

(14)

(15) R^1 = Me
(16) R^1 = Me, R^2 = CO_2Me
(17) R^2 = CO_2Me
(18) R^1 = Me, R^2 = OMe
(19) R^2 = OMe

(20)

(21) R^1 = Me
(22) R^1 = Me, R^2 = CO_2Me
(23) R^1 = Me, R^2 = OMe
(24) R^1 = R^3 = Me
(25) R^3 = Me
(26) R^1 = Bu^n, R^3 = Me
(27) R^1 = Me, R^3 = CH_2Ph
(28) R^1 = R^2 = R^3 = Me
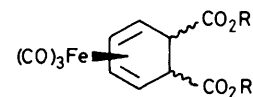
(29) β,β - $(CO_2Me)_2$
(30) β,β - $(CO_2H)_2$
(31) β,β - $(CO_2Me)_2$

inhibited by an adjacent α-substitution. Unchanged compound (3) was recovered and separated from tricarbonyl-(η^5-1-methoxycarbonyl-2-methylcyclohexadienyl)iron hexafluorophosphate. The isomer (2) was formed by borohydride reduction of the latter.

A similar sequence from 3-methylbenzoic acid led to the complex (4); complexes (5), (6), and (7) were prepared according to the literature.[5]

Dicarboxylic Esters.—For this study the complexes (22) [1,6β-(CO$_2$Me)$_2$], (16) [1,6α-(CO$_2$Me)$_2$], (29) [5β,6β-(CO$_2$Me)$_2$], and (31) [5α, 6β,(COαMe)$_2$] were available from benzene-1,2-dicarboxylic acid.[1] The 1,4-dimethoxycarbonyl complex (8) was obtained from dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate.[6] Results of the hydrolyses are shown in Table 1.

The lower rate of alkaline hydrolysis of 1-CO$_2$Me complexes, compared with the corresponding uncomplexed esters, must be due, therefore, to diminution of reactivity by electron-donation to the carbonyl group. This is supported by the raised pK_α of complexed diene acids.[10] The donation is presumably on demand from the Fe d-orbitals.

Alkaline hydrolysis of the 1,6β-dimethoxycarbonyl complex (22) resulted in the half-ester with 6α-CO$_2$H (17) (Table 1) with complete epimerization. A reaction with

TABLE 1

Alkaline hydrolysis of complex esters with an excess of aqueous (20%) NaOH–MeOH

Entry	Ester	Reaction conditions	Yield (%)	Product(s)
1	(1)	a	>95	(1)
2	(11)	a	94	(10)
3	(15)	a	85	(14)
4	(21)	a	75	(20) (major) + (1) + (15) (both minor)
5	(2)	a	>95	(2)
6	(3)	a	>95	(3)
7	(4)	a	>90	(4)
8	(5)	a	75	(5)
9	(6)	a	80	(6)
10	(7)	a	80	(7)
11	(16)	a	81	(17)
12	(8)	b	94	(9) + (36) (1 : 1)
13	(22)	a	74	(17)
14	(23) + (18) + (12) (5 : 6 : 9)	a	90	(13) + (19) (1 : 1)
15	(29)	a	80	(30)
16	(31)	a	76	(30)
17	(24)	c	40	(25)
18	(26) + (24) (1 : 3)	c	40	26) + (25) (1 : 3)
19	(27)	c	95	(27)
20	(28)	c	70	(28)

a 5—10 °C, 2 h.   *b* 5—10 °C, 1 h.   *c* 55—60 °C, 6 h.

In the 1,6α-dimethoxycarbonyl complex (16) only the 6α-CO$_2$Me group was hydrolyzed, which is consistent with the results above. However, one or both ester groups of the 1,4-dimethoxycarbonyl complex (8) were hydrolyzed, according to the conditions. The presence, therefore, of an electron-withdrawing substituent at the 4-position not unexpectedly enhances the rate of basic hydrolysis. Even so, the rate is much lower than with the uncomplexed diester, which is also impossible to stop cleanly at the monoester stage.

The effect of the Fe(CO)$_3$ group on the reactivity of a 1-CO$_2$Me group is not, primarily, a steric one. The Fe(CO)$_3$ group is approximately the same distance from the 1- and the 2-position [7,8] yet a 2-CO$_2$Me group is readily hydrolysed. Also the enhanced lanthanide induced shift (LIS) of the 1-CO$_2$Me group [9] in compounds (16) and (22) indicated no problem in the approach of the reagent and, also, probably a high degree of polarisation of the ester carbonyl to provide a more basic oxygen atom. The distances between the Fe and the C and O atoms of the 1-CO$_2$Me group are Fe–C 3.061 for compound (16) and 3.123 Å for compound (22), and Fe–O 3.887 and 4.070 Å, respectively,[7] and hence no direct bonding seems possible.

As expected, the acidic hydrolysis conditions used [3] on compound (1) were also successful with compound (17) and yielded the 1,2-dicarboxylic acid.

NaOD–D$_2$O–MeOD gave, after being quenched before complete hydrolysis, the 6α-acid which, however, lacked the dd at δ 3.46 which corresponds to the 6β-H of compound (17). The absence of the 6β-H was also manifest in the CH$_2$-5 splitting pattern; [9] the mass spectrum corresponds to 95% ^{2}H$_1$. The 6α-acid must therefore be compound (32) (Scheme). The neutral recovered ester was still the 6β-compound and contained 35% of α-^{2}H (^{1}H n.m.r. and mass spectroscopy). It results, presumably, from deuteriation of the mesomeric carbanion from the less hindered face to give what is still a resistant ester. Any 6α-CO$_2$Me group is presumably hydrolyzed as it is formed. The Scheme shows the probable course of reactions. On this basis, the isomerization of the 5β-CO$_2$Me (21) into compound (1) presumably involves abstraction of a proton to a mesomeric anion, without hydrolysis, and reprotonation at the other end. Once the 5β-CO$_2$Me group has been inverted to the 5α-position, the hydrolysis overwhelms the alternative abstraction reaction. Formation of the deuteriated ester (33) presumably proceeds as shown.

The 6α-H of compound (22) [1,6β-(CO$_2$Me)$_2$] was completely removed, while with compound (21) (5β-CO$_2$Me) this removal occurred only to a minor extent. The extra CO$_2$Me group has, therefore, a facilitating effect, possibly steric. The 1-CO$_2$Me complex (1) did not incorporate deuterium with NaOD–D$_2$O–MeOD and even

after prolonged reaction was recovered unchanged. This is a further indication of the unusual character of the CO_2Me group.

A group at C-1 might be expected to promote epimerization through the relief of steric strain. The only other example readily available was the 1-OMe in compound (23) which was produced mixed with compounds (18) and

blocked complexes with β-CO_2Me have been examined. The complexes (24), (27), and (28) were available [1,11] and the CO_2Bu^n complex (26) was present as a by-product in a preparation which had contained some BuOH in the dibutyl ether. The results are shown in Table 1.

The CO_2Me of the complexes is much more resistant to alkaline hydrolysis than the uncomplexed (but uncon-
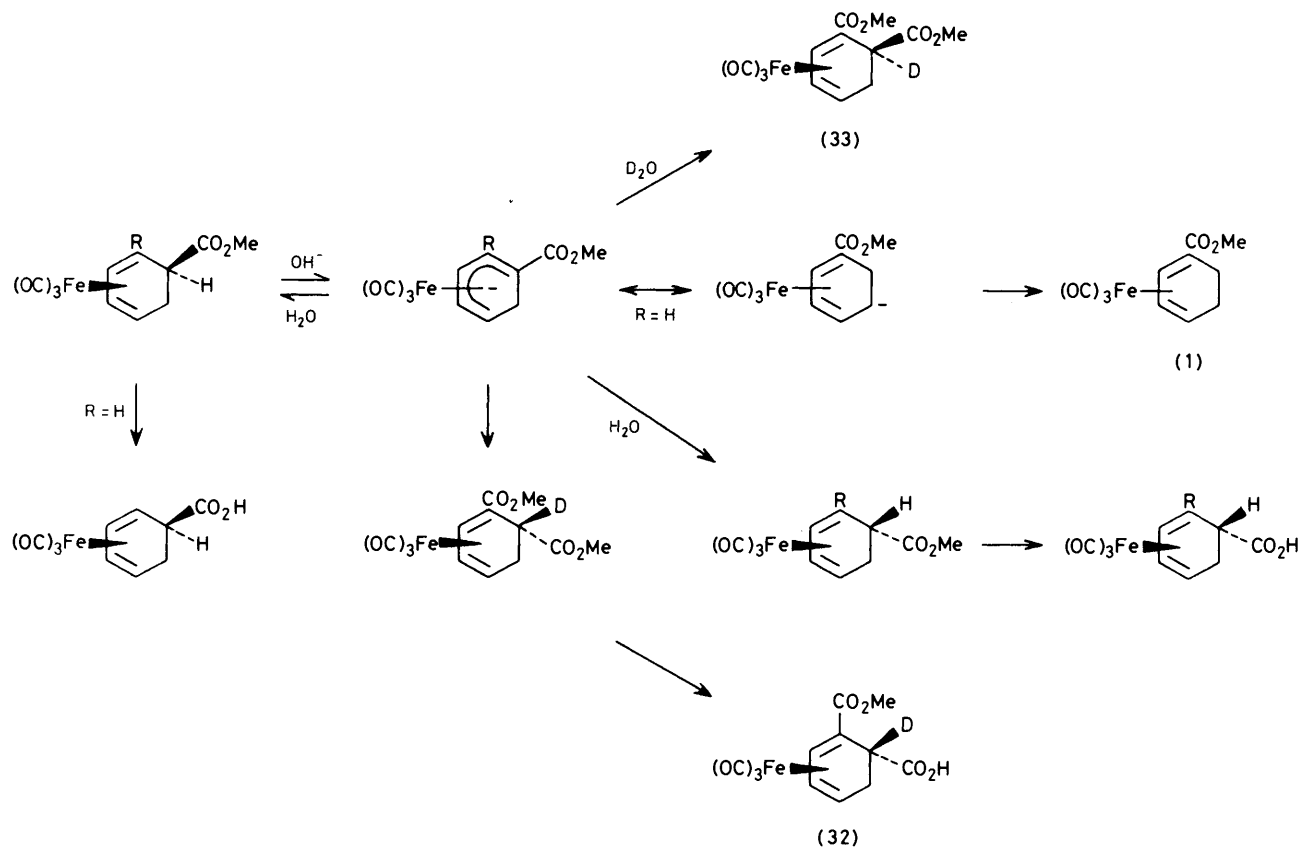
SCHEME Involvement of carbanions in the conversion of β-CO_2Me complexes into α-CO_2H and 1-CO_2Me complexes under alkaline hydrolysis

(12) (5 : 6 : 9).[1] The last two components were prepared from the corresponding acids and re-converted by hydrolysis into the salts of the corresponding acids in 87—93% yields. Hydrolysis of the mixture of three components gave, in 90% yield, a mixture of the two salts of the acids (19) (1-OMe, 6α-CO_2H) and (13) (1-OMe, 2-CO_2H) (1 : 1). No β-acid could be detected, and it is evident that epimerization of compound (18) occurred, more complete than in the ester which lacked OMe. Another example of promotion by steric interaction is the conversion of compound (29) into compound (30). The same acid results from complex (31).

X-Ray studies of (22) [7] show that the carbonyl carbon of the 6β-CO_2Me group is closer to the carbonyl carbon (2.943 Å) and the carbonyl oxygen (2.652 Å) of the 1-CO_2Me group than it is to Fe (2.945 Å) or the nearest CO of $Fe(CO)_3$ (3.594 Å).

Replacement of the H atom adjacent to CO_2Me will prevent epimerization and, accordingly, some such

jugated) diene starting materials. A larger alkoxy-group [compound (26)], or a bulky α-group [compound (27)] or additional Me at the 1-position [compound (28)] leads to the need for still more drastic conditions (see entries 18—20, Table 1). The $Fe(CO)_3$ seems to be exerting a classical hindrance effect to the approach of solvated hydroxyl anions and/or solvation of the ionic intermediate. Some organometallic reagents which produce preferential reactions on β-CO_2Me, probably via the $Fe(CO)_3$, will be discussed elsewhere.

A type of reaction of possible synthetic importance and an example of specific preference of α- over β-CO_2Me is the experimentally clean hydrolysis of the diester (34) to a monocarboxylic acid (35) without the necessity to take particular precautions. The expectation that the α-CO_2Me would be hydrolyzed in the product is supported by the disappearance of the higher field methoxycarbonyl signal ([1]H n.m.r. spectroscopy).[9]

The synthetic possibilities that the carboxy-function-

ality provides in these complexes include the formation of reactive intermediates such as acid chlorides,[12] decarbonylation to form cations,[13] and classical resolution of diene complexes through salts to provide chiral intermediates for asymmetric synthesis.[14] Removal of the $Fe(CO)_3$ from products of such processes should lead to organic products which are not readily possible in selective reactions of the uncomplexed series.
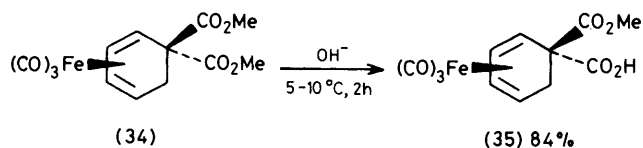
As one example of the formation of a purely organic product, the $Fe(CO)_3$ was removed from the complex (1) by the use of trimethylamine oxide and the ester was hydrolyzed to the acid. This is probably the easiest synthesis of cyclohexa-1,3-diene-1-carboxylic acid, in view of the use of benzoic acid as the starting material and the easy and good yield synthetic sequence.

Replacement of CO by larger and less electron-attracting groups such as phosphines or cyclopentadienyl should enhance the effects noted.

EXPERIMENTAL

For general conditions see the Experimental section in Part 11.[15]

Preparation of the Ester Complexes for Hydrolysis Studies.— The complexes (1),[3] (5), (6), (7),[5] (11),[3] (13),[4] (15), (16), (21), (22),[1] (24), (27),[1,11] (28),[1] (29), and (31)[1] were prepared according to literature.

Tricarbonyl-(η^4-1-methoxycarbonyl-3-methylcyclohexa-1,3-diene)iron (4). The complexation of methyl 4-methyl-cyclohexa-1,3-diene-2-carboxylate (2.75 g, 18 mmol) with pentacarbonyliron under thermal conditions [16] for 40 h gave, after normal work-up, a viscous yellow oil (3.65 g, 70%) which displayed spectroscopic properties consistent with the structure tricarbonyl-(η^4-3-methoxycarbonyl-1-methyl-cyclohexa-1,3-diene)iron; $\nu_{max.}$(film) 2 040, 1 975, and 1 720 cm^{-1}; δ (CDCl$_3$) 6.1 (1 H, s, 2-H), 3.82 (3 H, s, CO$_2$Me), 3.7 (1 H, m, 4-H), 2.1—2.2 (m, methylene H), and 1.66 (3 H, s, Me). The crude ester (2.0 g) was boiled in methanol (150 ml) that contained H$_2$SO$_4$ (15 ml) under reflux for 24 h.[3] Ice-cold brine was added to the cooled reaction mixture and the isomeric complex was extracted into light petroleum. The light petroleum extract was washed with water, dried (MgSO$_4$), and concentrated under reduced pressure. The resulting viscous yellow oil (2.0 g, 100%) was identified as *tricarbonyl-(η^4-1-methoxycarbonyl-3-methyl-cyclohexa-1,3-diene)iron* (4). It formed yellow crystals, m.p. 74—75 °C (from light petroleum); $\nu_{max.}$ (CHCl$_3$) 2 055, 1 980, and 1 700 cm^{-1}; δ (CDCl$_3$) 5.89 (1 H, s, 2-H), 3.65 (3 H, s, CO$_2$Me), 3.36 (1 H, m, 4-H), 2.08 (3 H, s, Me), and 2.05—1.28 (4 H, m, methylene H) (Found: M, 292.0035. Calc. for C$_{12}$H$_{12}$FeO$_5$: M, 292.0034).

Tricarbonyl (η^4-1-methoxycarbonyl-6α-methylcyclohexa-1,3-diene)iron (3). The application to 2-methylbenzoic acid of the reaction sequence metal/ammonia reduction–isomerization–methylation, complexation, and acid-catalyzed isomerization as above resulted, in a comparable yield, in a

viscous yellow oil which was identified by the reactions below as 1 : 1 mixture of tricarbonyl-(η^4-1-*methoxycarbonyl-6α-methylcyclohexa-1,3-diene)iron* (3) and tricarbonyl-(η^4-1-*methoxycarbonyl-2-methylcyclohexa-1,3-diene)iron* (2). This mixture could not be separated by conventional physical means. To the crude mixture of complexes (10.0 g, 34 mmol) was filtered in a solution of triphenylcarbenium hexa-fluorophosphate (13.3 g, 34 mmol) in acetonitrile (40 ml) which contained MgCO$_3$ (a few mg). After the dark brown solution had been stirred at ambient temperature for 30 min, a 2 : 1 mixture of diethyl ether and light petroleum was added to precipitate the resultant cationic salt, which was collected by filtration and dried under suction. The filtrate was reserved for isolation of the 6α-methyl complex (3). Recrystallisation of the yellow precipitate from MeCN–Et$_2$O–light petroleum gave a yellow crystalline solid (4.8 g, 11 mmol, 32%), identified as *tricarbonyl-(η^4-1-methoxycarbonyl-2-methylcyclohexadienylium)iron hexafluorophosphate*, decomp. >176 °C; $\nu_{max.}$ (KBr) 2 135, 2 090, 2 070, and 1 710 cm^{-1}; δ (CD$_2$CN) 7.17 (1 H, d, $J_{3,4}$ 5 Hz, 3-H), 5.84 (1 H, dd, $J_{4,5}$ 8 Hz, 4-H (1 H, dd, $J_{5,6\beta}$ 7 Hz, 5-H), 3.87 (3 H, s, CO$_2$-Me), 3.3 (1 H, dd, $J_{6\alpha,6\beta}$ 15 Hz, 6β-H), 2.5 (3 H, s, Me), and 2.07 (1 H, d, 6α-H) (Found: C, 33.3; H, 2.9. C$_{12}$H$_{11}$F$_6$Fe-O$_5$P requires C, 33.1; H, 2.5%).

The filtrate obtained above was concentrated and cooled (*ca.* −30 °C) to separate triphenylmethane. Distillation under reduced pressure gave a yellow oil (4.0 g, 14 mmol; 40%); b.p. 85—90 °C/0.1 mmHg (Kugelrhor); $\nu_{max.}$ (film) 2 050, 1 985, and 1 690 cm^{-1}; δ (CDCl$_3$) 6.06 (1 H, d, $J_{2,3}$ 4 Hz, 2-H), 5.42 (1 H, dd, $J_{3,4}$ 6 Hz, 3-H), 3.68 (3 H, s, CO$_2$-Me), 3.18 (1 H, m, $J_{4,5\beta}$ 3.5—4.0 Hz, $J_{4,6\alpha}$ 3.0 Hz, 4-H), 2.70 (1 H, m, 6β-H), 2.29 (1 H, m, $J_{5\alpha,5\beta}$ 16 Hz, $J_{5\beta,6\beta}$ 10 Hz, 5β-H), 1.44 (1 H, m,* 5α-H), and 0.88 (3 H, d, $J_{6\beta-Me}$ 6 Hz, Me (Found: M, 292.0036. Calc. for C$_{12}$H$_{12}$FeO$_5$: 292.0034).

Tricarbonyl-(η^4-1-methoxycarbonyl-2-methylcyclohexa-1,3-diene)iron (2). Tricarbonyl-(η^4-1-methoxycarbonyl-2-methylcyclohexadienylium)iron hexafluorophosphate (200 mg, 0.46 mmol) was added to a suspension of NaBH$_4$ (25 mg, 0.6 mmol) in MeCN (8 ml) at 0 °C and was stirred magnetically for 1 h. After addition of brine, the neutral complex was taken up in light petroleum and work-up as usual resulted in a viscous yellow oil (123 mg, 92%). The compound displayed physical properties consistent with the structure of tricarbonyl-(η^4-1-methoxycarbonyl-2-methylcyclohexa-1,3-diene)iron (2). An analytical sample was obtained by passage through a short column of basic alumina (activity 4) using light petroleum and diethyl ether (10%), b.p. 85—90 °C/0.1 mmHg (Kugelrohr); $\nu_{max.}$ (CHCl$_3$) 2 055, 1 990, and 1 690 cm^{-1}; δ (CDCl$_3$) 5.17 (1 H, d, $J_{3,4}$ 6—7 Hz, 3-H), 3.70 (3 H, s, CO$_2$Me), 3.19 (1 H, m, 4-H), 2.47 (3 H, s, Me), and 2.11—1.29 (4 H, m, methylene H) (Found: M, 292.0048. Calc. for C$_{12}$H$_{12}$FeO$_5$: M, 292.0034).

Tricarbonyl-(η^4-1,4-dimethoxycarbonylcyclohexa-1,3-diene)iron (8).—Dimethyl cyclohexa-1,3-diene-1,4-dicarb-oxylate was prepared from cyclohexane-1,4-dicarboxylic acid according to literature methods,[5] m.p. 84—85 °C (lit.,[5] m.p. 85—85.5 °C); δ (CDCl$_3$) 7.09 (2 H, s, diene H), 3.78 (6 H, s, 2 × CO$_2$Me), and 2.53 (4 H, s, methylene H). The diene ester (1.0 g, 4.9 mmol) and Fe(CO)$_5$ (1 ml) in Bu$_2$O (15 ml) was heated under reflux with occasional addition of Fe(CO)$_5$ [1 ml portions (×3), and a period of 30 h. The reaction mixture was cooled to room temperature before each addition and the mixture was brought to reflux gradually. Normal work-up afforded a homogeneous, yellow,

* CH$_3$ (α)-splitting pattern (ref. 9).

crystalline solid (1.67 g, 96%), m.p. 60—61 °C (from light petroleum); $\nu_{max.}$ 2 040, 1 995, and 1 697 cm^{-1}; δ (CDCl$_3$) 6.13 (2 H, s, 2- and 3-H), 3.72 (6 H, s, 2 × CO$_2$Me), 2.5—2.3 (2 H, m, 5β- and 6β-H), and 1.97—1.3 (2 H, m, 5α- and 6α-H); m/z 336 (M), 308 (M − CO), 280 (M − 2CO), and 252 (M = 3CO) (Found: C, 46.5; H, 3.6. C$_{13}$H$_{12}$FeO$_7$ requires C, 46.5; H, 3.6%).

Tricarbonyl-(η^4-5α,5β-dimethoxycarbonylcyclohexa-1,3-diene)iron (34).[11] Dimethyl cyclohexa-2,5-diene-1,1-dicarb-oxylate, prepared in 70% yield by addition of methyl chloroformate to the lithium enolate of methyl cyclohexa-2,5-dienecarboxylate using the method of Cregge *et al.*[17] was obtained as a liquid, b.p. 76—77 °C/0.15 mmHg; δ (CDCl$_3$) 5.8 (4 H, s, diene H), 3.67 (3 H, s, CO$_2$Me), 2.64 (2 H, s, methylene H), and 1.31 (3 H, s, Me). Complexation of the diene (6.0 g, 31 mmol) with Fe(CO)$_5$ (8 ml) under thermal conditions (see above) gave a viscous, yellow liquid (5.2 g), the ^{1}H n.m.r. spectrum of which indicated the presence of the required complex (34) contaminated with the starting diene (5%). The complex was purified by recrystalliz-ation from light petroleum at −18 °C to give the title *diester* (34) as yellow crystals (4.3 g, 42%), m.p. 56.5—57.5 °C; $\nu_{max.}$ (CDCl$_3$) 2 045, 1 980, and 1 740—1 720 cm^{-1}; δ (CDCl$_3$) 5.38 (2 H, m, 2- and 3-H), 3.73 (3 H, s 5β-CO$_2$Me), 3.63 (3 H, s, 5α-CO$_2$Me), 3.31 (1 H, d, $J_{3,4}$ 6 Hz, 4-H), 3.18 (1 H, m, 1-H), and 2.53—2.13 (2 H, m, 6-H); m/z 336 (M), 308 (M − CO), 280 (M − 2CO), and 252 (M − 3CO) (Found: C, 46.5; H, 3.3. C$_{13}$H$_{12}$FeO$_7$ requires C, 46.5; H, 3.6%).

Alkaline Hydrolysis of Esters.—*General procedure for alkaline hydrolysis.* An ice-cold solution (10 ml) of aqueous sodium hydroxide (20%) was added in small portions to an ice-cold solution of the ester (0.02 mol) in methanol (20 ml). The mixture was stirred magnetically at 5—10 °C for a further 2 h, diluted with water (75 ml), and washed with light petroleum (4 × 25 ml). The combined light petroleum extract was washed several times with water, dried (MgSO$_4$), concentrated under reduced pressure, and kept for identi-fication of the neutral component. The aqueous solution was acidified with ice-cold HCl (20%) and extracted with diethyl ether (4 × 25 ml). The combined diethyl ether extract was worked up as usual to obtain the acidic product.

Entries 1—4, Table 1. Tricarbonyl-(η^4-2-carboxycyclo-hexa-1,3-diene)iron (10), obtained from 2-CO$_2$Me complex (11), and tricarbonyl-(η^4-5α-carboxycyclohexa-1,3-diene)-iron (14), obtained from the 5α-CO$_2$Me complex (15), displayed the spectral properties reported previously.[1,2]

Alkaline treatment (as above) of tricarbonyl-(η^4-5β-methoxycarbonylcyclohexa-1,3-diene)iron (21) (500 mg, 1.8 mmol) gave a neutral (25 mg, 5%) and an acidic product (356 mg, 75%). The spectral properties of the former were consistent with a 1 : 1 mixture of the starting material (21) and tricarbonyl-(η^4-1-methoxycarbonylcyclohexa-1,3-diene)-iron (1). The ^{1}H n.m.r. spectrum of the acid product was a composite of the spectra of tricarbonyl-(η^4-5β-carboxy-cyclohexa-1,3-diene)iron (20) and the 5α-isomer (14).[1] The integration of the resonances at δ 2.57 [5-H of (21)] and δ 2.92 [5-H of (14)] indicated that compound (21) was the major product and compound (14) the minor product (<10%). Fractional recrystallization of the mixture of acids from CHCl$_3$ and light petroleum gave pure (21) [^{1}H n.m.r. spectroscopy, m.p. 116—119 °C (decomp.)][1] as the first crop.

Entries 5—10, Table 1. Only neutral product was ob-tained by the usual alkaline treatment of the esters (2)—(7)

which was shown, in each case, to be the unchanged starting material (^{1}H n.m.r. and i.r. spectroscopy).

Entries 11—13, Table 11. Tricarbonyl-(η^4-1,6α-di-methoxycarbonylcyclohexa-1,3-diene)iron (16) (1.5 g, 4.44 mmol) gave tricarbonyl-(η^4-6α-carboxy-1-methoxycarbonyl-cyclohexa-1,3-diene)iron (17) (1.152 g, 81%) only. Spectral data of compound (17) are reported elsewhere.[18] Tricar-bonyl-(η^4-1,6β-dimethoxycarbonylcyclohexa-1,3-diene)iron (22) gave the same acid (17).[18] A small amount of the un-changed ester (22) was noted (i.r. spectroscopy and t.l.c.) in the neutral fraction.

Tricarbonyl-(η^4-1,4-dimethoxycarbonylcyclohexa-1,3-diene)iron (8) (500 mg, 1.5 mmol) gave, under the usual hydrolysis conditions, a mixture of monocarboxy- and di-carboxy-complexes. The complex with the higher solu-bility in CHCl$_3$ was identified as *tricarbonyl-(η^4-1-carboxy-4-methoxycarbonylcyclohexa-1,3-diene)iron* (9) (297 mg, 65%), obtained as yellow crystals, m.p. 170—172 °C (from CHCl$_3$ and light petroleum; $\nu_{max.}$ (CHCl$_3$) 3 200—2 700br (CO$_2$H), 2 065, 2 000, and 1 700 cm^{-1}; δ (CDCl$_3$) 9.1br (1 H, s, CO$_2$H), 6.1 (2 H, s, 2- and 3-H), 3.71 (3 H, s, CO$_2$Me), 2.29 (2 H, m, 5β- and 6β-H), and 1.51 (2 H, m, 5α- and 6α-H); m/z 322 (M), 294 (M − CO), 266 (M − 2CO), and 238 (M − 3CO) (Found: C, 44.8; H, 3.2. C$_{12}$H$_{10}$FeO$_7$ requires C, 44.8; H, 3.1%).
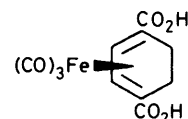
(36)

The complex less soluble in CHCl$_3$ was identified as tri-carbonyl-(η^4-1,4-dicarboxycyclohexa-1,3-diene)iron (36) (147 mg, 32%) which was also obtainable by further alkaline hydrolysis (NaOH–MeOH, room temperature, 2—3 h) of the monocarboxy-complex (9) as pale yellow crystals, decomp. >230 °C (from acetone); $\nu_{max.}$ (KBr) 3 350—2 350br (CO$_2$H), 2 075, 2 015, 1 990, and 1 710 cm^{-1}; δ(-[^{2}H$_6$]-DMSO) 11.0 (hump, CO$_2$H), 6.1 (2 H, s, 2- and 3-H), 2.15 (2 H, m, 5β- and 6β-H), and 1.49 (2 H, m, 5α-H and 6α-H) (Found: M, 307.9614. Calc. for C$_{11}$H$_8$FeO$_7$: M, 307.9619).

Entry 14, Table 1. The mixture [1] (10 g, 36 mmol) of tri-carbonyl-(η^4-1-methoxy-6β-methoxycarbonylcyclohexa-1,3-diene)iron (23), tricarbonyl-(η^4-1-methoxy-6α-methoxycar-bonylcyclohexa-1,3-diene)iron (18), and tricarbonyl-(η^4-1-methoxy-2-methoxycarbonylcyclohexa-1,3-diene)iron (12) (5 : 6 : 9) gave a neutral component (410 mg, 4%) and an acidic product (8.5 g, 90%). The t.l.c. of the neutral com-ponent indicated the presence of at least two compounds. The ^{1}H n.m.r. spectrum was a composite of those of tri-carbonyl-(η^4- 2-methoxy-1-methoxycarbonylcyclohexa-1,3-diene)iron (5) and tricarbonyl-(η^5-1-methoxycarbonylcyclo-hexa-1,3-diene)iron (1) in a ratio of 2 : 1. The ^{1}H n.m.r. spectrum of the acidic product (8.5 g, 90%) was a composite (1 : 1) of *tricarbonyl-(η^4-6α-carboxy-1-methoxycyclohexa-1,3-diene)iron* (19) and *tricarbonyl-(η^4-2-carboxy-1-methoxycyclo-hexa-1,3-diene)iron* (13) which were separated and identified as given below. The isomer ration (1 : 1) was estimated from the integration of the resonances at δ 5.88 [3-H of (13)], 5.5 [2-H of (19)], 5.16 [3-H of (19)], 3.64 [OMe of (13)], and 3.48 [OMe of (19)]. Fractional recrystallization from CHCl$_3$ and

light petroleum afforded compound (19) as less soluble yellow crystals (3.08 g, 38%), m.p. 150—152 °C (decomp.); $v_{max.}$ (CHCl$_3$) 3 300—2 500br (CO$_2$H), 2 045, 1 975, and 1 705 cm^{-1}; δ (CDCl$_3$) 9.1 (hump, CO$_2$H), 5.5 (1 H, d, $J_{2,3}$ 4.5 Hz, 2-H), 5.16 (1 H, dd, $J_{3,4}$ 6 Hz, 3-H), 3.38 (3 H, s, OMe), 3.39 (1 H, dd, $J_{5β,6}$ 10, $J_{5α,6}$ 4.Hz, 6-H), and 2.29—1.80 (2 H, m,* 5-H) (Found: M, 265.9876. Calc. for C$_{10}$H$_{10}$FeO$_5$: M, 265.9877).

The second crop (2.1 g, 25%) from recrystallization contained both compounds (13) and (19) in a ratio of 1 : 1 (^{1}H n.m.r. spectroscopy).

The third crop (1.1 g, 12%) displayed spectral properties consistent with the structure of tricarbonyl-($η^4$-2-carboxy-1-methoxycyclohexa-1,3-diene)iron (13), decomp. >180 °C; $v_{max.}$ (CHCl$_3$) 3 300—2 500br (CO$_2$H), 2 050, 1 980, and 1 710 cm^{-1}; δ (CDCl$_3$) 9.0 (hump, CO$_2$H), 5.94 (1 H, d, $J_{3,4}$ 6.5 Hz, 3-H), 3.66 (3 H, s, OMe), 3.32 (1 H, m, 4-H), and 2.2—1.8 (4 H, m, 5- and 6-H) (Found: M, 265.9873. Calc. for C$_{10}$H$_{10}$FeO$_5$: M, 265.9877).

Methylation (Me$_2$SO$_4$) of the acids (19) (1-OMe, 6α-CO$_2$H) and (13) (1-OMe, 2-CO$_2$H) gave, in good yield (85—90%), tricarbonyl-($η_4$-1-methoxy-6-methoxycarbonylcyclohexa-1,3-diene)iron (18)[4] and tricarbonyl-($η_4$-1-methoxy-2-methoxycarbonylcyclohexa-1,3-diene)iron (12),[4] respectively.

Alkaline hydrolysis of compound (18) afforded, in 87% yield, only compound (19) (^{1}H n.m.r. spectroscopy). Similarly, compound (12) gave, in 93% yield, compound (13) only (^{1}H n.m.r. spectroscopy).

Entries 15 and 16, Table 1. Tricarbonyl-($η^4$-5β,6β-dimethoxycarbonylcyclohexa-1,3-diene)iron (29) (200 mg, 0.6 mmol) gave *tricarbonyl-($η^4$-5α-6β-dicarboxycyclohexa*-1,3-*diene*)*iron* (30) (148 mg, 80%) as pale yellow crystals, decomp. >165 °C (from acetone and CHCl$_3$); $v_{max.}$ (Nujol) 3 300—2 600br (CO$_2$H), 2 050, 1 965, and 1 700 cm^{-1}; δ ([^{2}H$_6$]acetone) 9.8 (hump, CO$_2$H), 5.55 (2 H, m, 2- and 3-H), 3.30 (3 H, m, 1-, 4-, and 6-H), and 2.90 (1 H, narrow m, 5-H); m/z 280 (M — CO), 252 (M — 2CO), and 224 (M — 3CO) (Found: C, 42.8; H, 2.6. C$_{11}$H$_{18}$FeO$_7$ requires C, 42.9; H, 2.6%).

Under similar conditions tricarbonyl-($η^4$-5α,6β-dimethoxy-carbonylcyclohexa-1,3-diene)iron (31) gave, in 76% yield, the same dicarboxy-complex (30) (i.r. and ^{1}H n.m.r. spectroscopy).

Entries 17—20, Table 1. Tricarbonyl-($η^4$-5β-methoxy-carbonyl-5α-methylcyclohexa-1,3-diene)iron (24), the 3 : 1 mixture of compound (24) and tricarbonyl-($η^4$-5β-n-butoxy-carbonyl-5-methylcyclohexa-1,3-diene)iron (26), tricarbonyl-($η^4$-5α-benzyl-5β-methoxycarbonylcyclohexa-1,3-diene)iron (27), and tricarbonyl($η^4$-6β-methoxycarbonyl-1,6α-dimethylcyclohexa-1,3-diene)iron (28) were recovered unchanged (^{1}H n.m.r. spectroscopy), under the usual hydrolysis conditions (5—10 °C, 2 h). The latter two compounds (27) and (28) did not react even at 55—60 °C (6 h).

Tricarbonyl-($η^4$-5β-methoxycarbonyl-5α-methylcyclo-hexa-1,3-diene)iron (24) (250 mg, 0.86 mmol) at 55—60 °C (6 g) gave tricarbonyl-($η^4$-5β-carboxy-5α-methylcyclohexa-1,3-diene)iron (25) (95 mg, 40%) as yellow crystals, m.p. 135—136 °C (from CHCl$_3$ and light petroleum); $v_{max.}$ (CHCl$_3$) 3 300—2 400br (CO$_2$H), 2 050, 1 985, and 1 700 cm^{-1}; δ (CDCl$_3$) 11.27br (1 H, s, CO$_2$H), 5.32 (2 H, m, 2- and 3-H), 3.36 (1 H, dd, $J_{3,4}$ 6, $J_{2,4}$ 2.5 Hz, 4-H), 3.08 (1 H, m, 1-H), 2.61 (1 H, dd, $J_{6α,6β}$ 16, $J_{1,6β}$ 4 Hz, 6β-H), 1.54 (1 H, dd,

* CH$_2$ (α)-splitting pattern corresponds to $Δδ < 0.35$ (ref. 9).

$J_{1,6α}$ 3 Hz, 6-H), and 1.26 (3 H, s, Me); m/z 250 (M — CO), 222 (M — 2CO), and 194 (M — 3CO) (Found: C, 47.6; H, 3.7. C$_{11}$H$_{10}$FeO$_5$ requires C, 47.5; H, 3.6%). A significant amount of brownish residue was observed due to decomposition in the course of the reaction.

The mixture (3 : 1) of the 5β-methoxycarbonyl complex (24) and the 5β-n-butoxycarbonyl complex (26) was obtained as a minor chromatographic fraction in one preparation of compound (24), using Bu$^n_2$O accidentally contaminated with butanol and a trace amount of mineral acid. When this mixture (450 mg) was subjected to alkaline hydrolysis (55—60 °C, 6 h), the neutral product (52 mg, 0.16 mmol) displayed spectral properties consistent with the structure of *tri-carbonyl-($η^4$-5β-butoxycarbonyl-5α-methylcyclohexa*-1,3-*diene*)*iron* (26); $v_{max.}$ (CHCl$_3$) 2 055, 1 975, and 1 730 cm^{-1}; δ (CDCl$_3$) 5.31 (2 H, m, 2- and 3-H), 4.09 (2 H, t, $J_{1',2'}$ 6 Hz, OCH$_2$), 3.40 (1 H, dd, $J_{2,4}$ 2, $J_{3,4}$ 6 Hz, 4-H), 3.08 (1 H, m, 1-H), 2.60 (1 H, dd, $J_{1,6β}$ 3.5, $J_{6α,6β}$ 16 Hz, 6β-H), 1.70—1.36 (5 H, m, 6α-, 2 × 2'- and 2 × 3'-H), 1.20 (3 H, s, Me), and 0.94 (3 H, t, $J_{3',4'}$ 6.5 Hz, 3 × 4'-H); m/e 334 (M), 306 (M — CO), 278 (M — 2CO), and 250 (M — 3CO). The acidic product (130 mg, 0.47 mmol) was identified as (25) (i.r. and ^{1}H n.m.r. spectroscopy).

Tricarbonyl-($η^4$-5α-carboxy-5β-methoxycarbonylcyclo-hexa-1,3-diene)iron (35) (241 mg, 84%), obtained from tri-carbonyl-($η^4$-5α,5β-dimethoxycarbonylcyclohexa-1,3-diene)-iron (34) (300 mg, 0.89 mmol) gave spectra reported elsewhere.[12]

Uncomplexed Diene Ester.—*Cyclohexa*-1,3-*dienecarboxylic acid.* A mixture of tricarbonyl-($η^4$-1-methoxycarbonyl-cyclohexa-1,3-diene)iron (1) (700 mg, 2.5 mmol) and tri-methylamine N-oxide dihydrate (2.0 g, 18 mmol) in NN-dimethylacetamide (15 ml) was stirred at ambient temperature for 10 h. The reaction mixture was filtered through Celite, which was washed through with water and light petroleum. The light petroleum extract of the diene ester was washed with water, dried (MgSO$_4$), and concentrated to give crude methyl cyclohexa-1,3-dienecarboxylate [18] (200 mg, 58%) yield) (contaminated with a trace amount of aromatic material); δ 6.96 (1 H, d, J 5 Hz, 2-H), 6.06 (2 H, m, 3- and 4-H), 3.73 (3 H, s, CO$_2$Me), and 2.3 (4 H, m, methylene). Alkaline hydrolysis (5—10 °C, 2 h) afforded cyclohexa-1,3-dienecarboxylic acid (140 mg, 78%); $v_{max.}$ (CHCl$_3$) 3 500—2 500br (CO$_2$H), 1 685, and 1 590 cm^{-1}; δ (CDCl$_3$) 12.1 (s, CO$_2$H), 7.1 (1 H, d, J 5 Hz, 2-H), 6.11 (2 H, m, 3- and 4-H), and 2.37 (4 H, m, methylene).

Cyclohexa-1,3-*diene*-1,4-*dicarboxylic acid.* Dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (150 mg, 0.77 mmol), prepared as above, was subjected to the alkaline hydrolysis conditions (5—10 °C, 2 h) used for partial hydrolysis of the complex to yield cyclohexa-1,3-diene-1,4-dicarboxylic acid as the only product (119 mg, 92%), m.p. 348—351 °C (lit.,[6] 349—351 °C); δ ([^{2}H$_6$]DMSO) 12.0 (2 H, hump, CO$_2$H), 7.0 (2 H, s, diene H), and 2.46 (4 H, s, methylene).

1-*Benzylcyclohexa*-2,5-*diene*-1-*carboxylic acid.* Methyl 1-benzylcyclohexa-2,5-dienecarboxylate (200 mg, 0.88 mmol) was subjected to alkaline hydrolysis (room temperature, 2 h) to give 1-benzylcyclohexa-2,5-diene-1-carboxylic acid (176 mg, 94%); $v_{max.}$ 3 500—3 400br (CO$_2$H), 1 700s, 1 635w, and 1600w; δ (CDCl$_3$) 11.89 (1 H, s, CO$_2$H), 7.19 (5 H, s, Ph), 5.93 (4 H, s, diene H), 3.02 (2 H, s, CH_2Ph), and 2.42 (2 H, m, methylene).

Under similar conditions, methyl 1-methylcyclohexa-2,5-dienecarboxylate afforded the corresponding 2,5-diene acid [19] in 87% yield.

Treatment of Tricarbonyl-(η^4-1,6β-dimethoxycarbonylcyclohexa-1,3-diene)iron (22) and Tricarbonyl-(η^4-1-methoxycarbonylcyclohexa-1,3-diene)iron (1) with NaOD–D$_2$O–MeOD.— Sodium (115 mg, 5 mmol) was added to ice-cold MeOD (5 ml). To this solution was added D$_2$O (2 ml) as drops at 0 °C. The diester complex (22) (45 mg, 0.13 mmol), dissolved in MeOD (1 ml), was added to the alkaline solution and the reaction mixture was stirred magnetically at 5—10 °C for 1 h. The reaction mixture was worked up as described above. The neutral component (14 mg, 31%) displayed i.r. and t.l.c. characteristics identical with those of the diester (22); δ (CDCl$_3$) 5.91 (1 H, dt, $J_{2.3}$ 4.5, $J_{2.4}$ 1 Hz, 2-H), 5.31 (1 H, dd, $J_{3.4}$ 6.5 Hz, 3-H), 3.68 (3 H, s, 1-CO$_2$Me), 3.63 (3 H, s, 6β-CO$_2$Me), 3.41 (1 H, m, 4-H), 2.35 (*ca.* 0.5 H, 6-H), and 2.26—1.5 (2 H, m, 5α- and 5β-H). Mass spectroscopic analysis indicated [^{2}H$_1$]-incorporation of 35%). These spectral properties were consistent with a composite of compound (22) and tricarbonyl-(η^4-1,6α-dimethoxycarbonyl-[6α-^{2}H$_1$]cyclohexa-1,3-diene)iron (34).

The acidic component (23 mg, 55%) was identified as *tricarbonyl-(η^4-6α-carboxy-1-methoxycarbonyl[6β-^{2}H$_1$]cyclohexa-1,3-diene)iron* (33); $\nu_{max.}$ (CHCl$_3$) 3 500—2 300br (CO$_2$H), 2 035, 1 987, and 1 700 cm^{-1}; δ (CDCl$_3$) 9.1 (hump, CO$_2$H), 6.21 (1 H, d, $J_{2.3}$ 4.5 Hz, 2-H), 5.43 (1 H, dd, $J_{3.4}$ 7.5 Hz, 3-H), 3.67 (3 H, s, CO$_2$Me), 3.23 (1 H, m, 4-H), 2.40 (1 H, dd, $J_{5\alpha.5\beta}$ 15.5, $J_{4.5\beta}$ 3.7 Hz, 5β-H), and 1.91 (1 H, dd, $J_{4.5\alpha}$ 2.8 Hz, 5α-H). Mass spectroscopic analysis indicated 95% monodeuterium incorporation.

Under similar condition with NaOD–D$_2$O–MeOD, tricarbonyl-(η^4-1-methoxycarbonylcyclohexa-1,3-diene)iron (1) was isolated unchanged (i.r., ^{1}H n.m.r. and mass spectra). No deuterium incorporation was observed even after prolonged reaction conditions (room temperature, 6 h).

Acidic Hydrolysis of Tricarbonyl-(η^4-6α-carboxy-1-methoxycarbonylcyclohexa-1,3-diene)iron (17).—A suspension of the monocarboxy-ester (17) (450 mg, 1.4 mmol) in 20% H$_2$SO$_4$ (50 ml) was boiled under reflux for 24 h. The reaction mixture was cooled and diluted with water (*ca.* 50 ml). The solid material in the mixture was extracted into diethyl ether (*ca.* 25 ml × 4). The combined diethyl ether extract was washed several times with water, dried, and concentrated to give a pale yellow solid (398 mg, 92%) which had spectral properties consistent with the structure of *tricarbonyl-(η^4-1,6α-dicarboxycyclohexa-1,3-diene)iron*, obtained as pale yellow crystals, decomp. > 216 °C (from acetone and

* CH$_2$(α)-splitting pattern (ref. 9).

CHCl$_3$); $\nu_{max.}$ (KBr) 2 060, 1 990, and 1 705 cm^{-1}; δ(^{12}H$_6$]-acetone) 6.28 (1 H, d, $J_{2.3}$ 4.5 Hz, 2-H), 5.68 (1 H, dd, $J_{3.4}$ 6.0 Hz, 3-H), 3.40 (2 H, m, 4- and 6-H), 2.43 (1 H, m,* 5β-H), and 1.90 (1 H, m, 5α-H); m/z 308 (M), 280 (M − CO), 252 (M − 2CO), and 224 (M − 3CO) (Found: C, 43.0; H, 2.9; C$_{11}$H$_8$FeO$_7$ requires C, 42.9; H, 2.6%).

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