Organometallic Compounds in Organic Synthesis. Part 13.[1] Stereoselectivity of Complexation of Cyclohexadiene Esters

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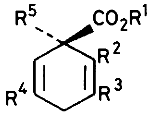
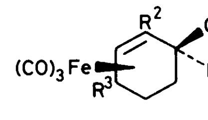
Complexation of cyclohexadienes with $Fe(CO)_3$ as the entering group are subject to classical steric hindrance by alkyl groups, but CO_2R and related groups introduce a competing factor because they favour sterically the entering group, probably through an intermediate complex. Increase of π-electron availability in the initial 1,4-diene by the attachment of OMe reduces this influence, probably because it favours direct olefin complexation. Non-polar conditions increase the directing effect of CO_2R, but complete stereospecificity cannot be achieved except through additional alkyl substitution. Nevertheless, many stereoisomeric pairs can be separated and the route leads to precursors of a number of sterically defined products which are otherwise not readily accessible.

SUBSTITUTED tricarbonyldieneiron complexes need to be available in pure form, structurally and sterically, if they are to be used as synthetic intermediates. Reactions of substituted cyclohexa-1,4-dienes (from the Birch reduction of the aromatic analogues) with iron carbonyl groups usually result in a mixture of structures in the complexes, but also with the predominant stereoisomers, if these are possible, having the less crowded α-substituent.[2] The more crowded β-CO_2Me substituent has, however, been noted [3,4] in the major product obtained from compound (1), which implies an interaction between the ester function and the entering $Fe(CO)_n$.[5] A similar interaction has been reported in another series.[6] Further examination of the course of such reaction has now been facilitated by our ability to separate most of the products.

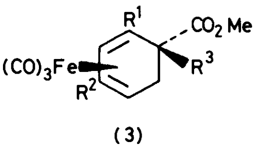
All $R^n = H$ unless stated otherwise



(1) $R^1 = Me$
(5) $R^1 = CH_2COC_6H_4Br—p$
(7) $R^1 = Me$, $R^3 = R^4 = OMe$
(9) $R^1 = R^5 = Me$, $R^3 = R^4 = OMe$
(12) $R^1 = Me$, $R^2 = OMe$
(16) $R^1 = Me$, $R^2 = CO_2Me$

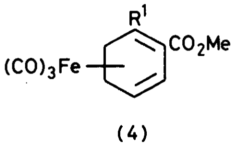


(2) $R^1 = Me$
(6) $R^1 = CH_2COC_6H_4Br—p$
(10) $R^1 = R^4 = Me$, $R^2 = R^3 = OMe$
(13) $R^1 = Me$, $R^2 = OMe$



(3)

(8) $R^1 = R^2 = OMe$
(11) $R^1 = R^2 = OMe$, $R^3 = Me$



(4)

(15) $R^1 = OMe$

Further studies were undertaken to establish the extent to which defined products are obtained and whether experimental identification of the desired isomers is possible.

RESULTS AND DISCUSSION

The reaction of the diene (1) with pentacarbonyliron has been reported [3] to yield a mixture of compounds (2), (3), and (4). Initial complexation of the reactive iron species with the ester group has been suggested [3,5] to explain the preferential formation of the more sterically crowded isomer (2). A possible mode of formation of the other products is through isomerization of compound (2) during the process. To test possible isomerizations, the pure component esters were needed.

The 5β-CO_2Me complex (2) could not be completely separated directly by conventional methods; including chromatography on $AgNO_3$-impregnated silica. Separation was, however, indirectly accomplished by fractional crystallization of the mixture of carboxy-complexes obtained by alkaline hydrolysis of the ester mixture. The pure esters were then obtained by methylation with methyl sulphate of the salts. Structures were confirmed by ^1H n.m.r. spectroscopy [1] and by the fact that compound (2) is subject to hydride abstraction by trityl cation whereas compound (3) is not. The isomer (4) is obtainable directly from the readily available diene.[4]

When subjected to the conditions used to form a complex with compound (1) these esters were all unchanged. They represent, therefore, kinetically determined products, produced by co-ordination of $Fe(CO)_n$ (where $n = 3$ [7] or 4 [8]) with one of the double bonds of compound (1) and transformations of the subsequent π-allyl intermediates (compare with Scheme 1). Studies with acyclic dienes [8a] also suggest kinetic control of products.

The preferred conformation of cyclohexa-1,4-diene has been shown [9] to be nearly planar by using homoallylic coupling constants. We make the same assumption from the homoallylic couplings of between 7.5 and 8.3 Hz given by the dienes used in this study.

The approach of the co-ordinately unsaturated iron species to the olefinic bonds of the planar cyclohexa-1,4-diene will be subject to steric hindrance by any group replacing a hydrogen atom of CH_2.[2] Complexation would then be expected to take place on the opposite face predominantly, as is well known with the 1,3-diene 'α'-phellandrene.[2] Since this is not true of the substituent CO_2Me, some other directing factor must operate, probably interaction of the entering group with the carbonyl group, thus directing to the same face. The mechanism of formation of the complex corresponding to the conjugated diene is probably the transfer of β-H *via* the Fe atom which involves π-allyl intermediates.[10] A structural requisite for conjugation is therefore a β-H atom, which is found only in the 4-position of the β-isomer (2), but in both the 1- and the 4-positions in the intermediate which gives compounds (3) and (4). The approximately equal ratios of compounds (3) and (4) obtained (see Table) suggests that, despite the polar nature of CO_2Me, the selectivity is low. The ratio of compound (2) to the combined isomers (3) and (4) represents, in these mechanisms, the ratio of initial attack on the same side and on the opposite side of the CO_2Me group.

TABLE

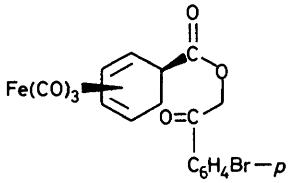
Product distribution in the reaction of methyl cyclohexa-2,5-dienecarboxylate (1) with $Fe(CO)_5$ under different conditions

Reaction conditions	Yield (%) [a]	Isomer ratio [b] (2) : (3) : (4)
Bu^n_2O, reflux, 18 h	50 [c]	74 : 13 : 13
Bu^n_2O, reflux, 20 h	56 [c]	70 : 15 : 15
Bu^n_2O, reflux, 36 h	30	60 : 10 : 30
Bu^n_2O, reflux, 18 h	56 [c,d]	80 : 10 : 10
Et_2O, *hν*, 4 h	43	75 : 15 : 10
C_6H_{14}, *hν*, 4 h	27	70 : 15 : 15
MeOH, *hν*, 2 h	7	50 : 25 : 25
Bu^nOH, *hν*, 18 h	2	50 : 25 : 25

[a] The yield after distillation at 80—82 °C/0.01 mmHg. [b] Isomer ratio was calculated from ^1H n.m.r. spectra. Recovered diene and $Fe(CO)_5$ from the first run were reacted again. [d] $Fe(CO)_5$ in Bu^n_2O was added as drops to the diene in Bu^n_2O, with stirring, while the reaction mixture was brought to reflux over a period of *ca.* 4 h.

The complexation of compound (1) was examined (see Table) for the effects of conditions on yields and on isomer ratios. Reaction time does not have any significant effect on isomer ratios, although prolonged heating causes extensive decomposition and reduces the yield. There is also little difference between the thermochemical method and irradiation. In the more polar solvent methanol the yield is very poor and the proportion of the 5β-isomer is reduced, which indicates that the hindrance effect of the substituent is taking over from ester complexing, possibly due to complexation of $Fe(CO)_n$ with the solvent.

To find out whether an increase in the polar character of the ester group can usually influence the ratio, *p*-bromophenacyl cyclohexa-2,5-dienecarboxylate (5) was investigated. A method of Durst[11] proved the most satisfactory for esterification of the acid: other methods[12] gave larger amounts of aromatic products. The diene (5) treated with $Fe(CO)_5$ under thermal conditions gave a complex mixture of products, which contained a low yield of the desired product (6) (^1H n.m.r. spectroscopy).[1] Assignment of the β-configuration was confirmed by reaction with Zn–HAc[12] to give the acid, which was esterified to the known β-ester (2). Although more selective, the yield is too poor to make the approach of any practical interest.



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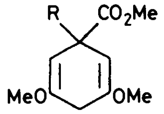
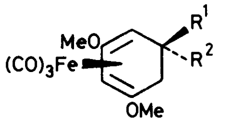


(7) R=H

(9) R=Me



(8) $R^1 = H$, $R^2 = CO_2Me$

(10) $R^1 = CO_2Me$, $R^2 = Me$

(11) $R^1 = Me$, $R^2 = CO_2Me$

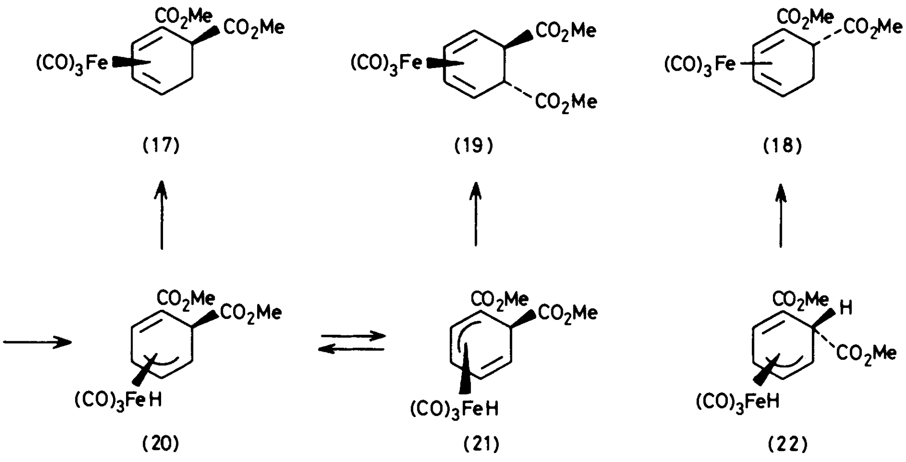
A reversal of stereoselectivity compared with compound (1) was observed on complexing the dimethoxy-diene (7). The product is mainly compound (8) with only traces of other complexes. The structure was assigned by the coupling constant of the two β-protons (*J* 11 Hz) and the chemical shifts of 5β-H (δ 2.90) and 5α-CO_2Me (δ 3.58).[1] It is also resistant to hydride abstraction.

More detailed investigation of the previously reported[3] methyl 2-methoxycyclohexa-2,5-dienecarboxylate (12) showed the three complexation products (13) (1-OMe, 6β-CO_2Me), (14) (1-OMe, 6α-CO_2Me), and (15) (1-OMe, 2-CO_2Me) in ratios of 5 : 6 : 9 (^1H n.m.r. spectroscopy). The complexes (14) and (15) must arise from attack of $Fe(CO)_n$ on the face opposite to CO_2Me. The β-approach yields what is now only the minor isomer (13). The case is intermediate between compound (1) which lacks an OMe group and compound (7) with two OMe groups.

The dimethoxy-diene (9), in which the geminal Me,CO_2Me grouping presents a substituent on both faces, gave equal proportions of the β-CO_2Me compound (10) and its isomer (11). The corresponding diene which lacked an OMe group gave, as discussed below, only the β-isomer (29).

These results suggest that when the π-electron availability of the C=C double bond is increased by the presence of OMe the co-ordinately unsaturated $Fe(CO)_n$ attaches itself directly. That compounds (7) and (9) retain the OMe group in the process contrasts with the dimethoxy-diene that lacks the CO_2Me group, which gives monomethoxy-complexes.[13] The migration of unsaturation needed for removal must be inhibited by the ester group.

To investigate the effect of an additional electron-withdrawing substituent, which could show both steric and electronic effects, and the products of which should present two functional groups for further syntheses, the dicarboxylate (16) was prepared from *trans*-cyclohexa-3,5-diene-1,2-dicarboxylic acid.[14] This ester, under thermal conditions with $Fe(CO)_5$, gave 74—93% of a mixture of the three complexes (17) [1,6β-$(CO_2Me)_2$], (18) [1,6α-$(CO_2Me)_2$], and (19) [5α,6β-$(CO_2Me)_2$] (1 : 3 : 1). Comparison of the ^1H n.m.r. spectrum of the mixture with an artificial spectrum composed of the separated components revealed no evidence of other isomers. The use of xylene as solvent instead of di-n-butyl ether gave a lower yield (30%) and a ratio of 4 : 7 : 4, respectively.



SCHEME

Initial complexation could occur through either ester group or directly with the olefinic bonds. The C=C double bond with CO_2Me attached should have less π-availability, but any complex formed is likely to be more stable than that with the unsubstituted bond because of increased back-bonding.

Both compounds (17) and (19) (see the Scheme) could arise as shown from the pair of interconverting allyl complexes[2] (20) and (21) which arise initially by complexation on the same face as the allylic CO_2Me group. The major product (18) could most readily arise from an intermediate of type (22) which could have originated by addition through $C=CCO_2Me$. However, other routes involving β-H transfer are possible. It is of practical interest that no products are obtained which have the CO_2Me groups *cis* to each other or attached to two adjacent unsaturated carbons; this is presumably for steric reasons. The factors that determine, in general, the nature of products is not clear; the products themselves are stable except under drastic conditions; the stabilities and transformations of the intermediate allylic complexes are probably decisive.

The effects of the Me group in the carboxylate (23) were difficult to elucidate because of the complexity of the mixed product. By removing one of the H atoms, which can migrate, the number of π-allyl intermediates should be reduced. We have accordingly examined some 1-blocked cyclohexa-1,4-dienecarboxylic esters. Some preliminary results have been noted.[5]

The dienes (24)—(28) were prepared by the Birch reductive alkylation[15] in liquid ammonia of some benzoic acids, followed by esterification of the salts with methyl sulphate. Complexation gave only the β-CO_2Me group in the series (29)—(33). The structures are supported by spectra; in addition the β-configuration of the CO_2Me group is attested by resistance to alkaline hydrolysis.[16] This result suggests that a combination of steric hindrance by the substituent and complexation with the ester results in complete specificity. With an alkyl group alone, as in 'α'-phellandrene[2] there is a ratio of 4 : 1 for α-Pr^i : β-Pr^i.

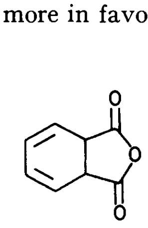
In contrast to the OMe group, the Me group seems to be insufficient to activate the C=C double bond in competition, since compounds (27) and (28) do not give rise to any β-CO_2Me product. However, the Me group is apparently sufficient to decide between the two double bonds in competition for the transferred group; in the products only the unsubstituted double bond moves into conjugation.

(23) $R^1 = R^3 = H$, $R^2 = Me$

(24)	$R^1 = Me$, $R^2 = R^3 = H$	(29)
(25)	$R^1 = CH_2Ph$, $R^2 = R^3 = H$	(30)
(26)	$R^1 = CH_2C_6H_3(OMe)_2$-*m*, $R^2 = R^3 = H$	(31)
(27)	$R^1 = R^2 = Me$, $R^3 = H$	(32)
(28)	$R^1 = R^3 = Me$, $R^2 = H$	(33)

To separate the conjugation step from the complexation, we have examined several preformed 1,2-dienes.

Also, in order to discover whether another group might have the same kind of directive effects we have examined the 1,2-dicarboxylic anhydride (34).[17] The product, obtained in low yield under photochemical conditions, was a mixture of the β- and α-complexes (35) and (36) (4 : 1). Ennecarbonyldi-iron in refluent butan-2-one produced the same compounds, but in a different ratio (1 : 2), more in favour of the less compressed α-complex (36).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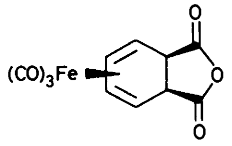

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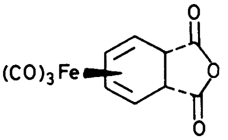

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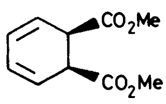

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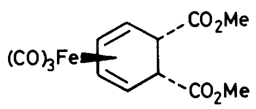

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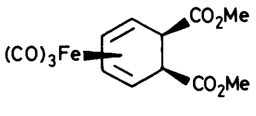

(38)

Complexation of the *cis*-diester (37)[18] under photochemical conditions gave a good yield of the β- and α-isomers (38) and (39) (2 : 1). This provides a particularly clear example of formation of the more crowded isomer.

Many of the compounds discussed can exist as enantiomers, but the formulae given are arbitrarily chosen to represent both enantiomers of the (±)-structure.

EXPERIMENTAL

For general conditions see the Experimental section in Part 11.[19]

General Procedure for Complexation of Dienes with Pentacarbonyliron.—Complexation was performed under 'thermal' or 'photochemical' conditions. The thermal reaction, unless specified otherwise, involved boiling the diene with an excess of filtered pentacarbonyliron (*ca.* 2.0—3.0 mol equiv.) in di-n-butyl ether (freshly filtered through basic alumina; *ca.* 10 ml for 1 g of diene) under reflux for 18—20 h.[3, 4] After being cooled to the ambient temperature, the reaction mixture was filtered through Celite and the solvent removed, together with any excess of $Fe(CO)_5$, under aspirator pressure (*ca.* 12 mmHg, 60—70 °C). The residue was passed through a short column of silica gel H (type 60), using a mixture of diethyl ether and light petroleum (1 : 1) as the eluant. Unchanged diene (if any present) was removed by recrystallization or distillation under reduced pressure; in the case of some blocked ester complexes the unchanged diene was removed by alkaline hydrolysis when the complex remained unchanged.

The photochemical method involved irradiation, under reflux, of the mixture of the diene, pentacarbonyliron, and the solvent with ultraviolet light from Clemco 16 × 12 W u.v. lamp (280 nm). The work-up was similar to that described above.

Separation of the Mixture of Tricarbonyl-(η^4*-5β-methoxycarbonylcyclohexa-*1,3*-diene)iron* (2), *Tricarbonyl-*(η^4*-5α-methoxycarbonylcyclohexa-*1,3*-diene)iron* (3), *and Tricarbonyl-*(η^4*-2-methoxycarbonylcyclohexa-*1,3*-diene)iron* (4).—Complexation of methyl cyclohexa-2,5-dienecarboxylate (1)[4] under thermal conditions produced a mixture of compounds (2), (3), and (4), in a ratio of 14 : 3 : 3 (^1H n.m.r. spectroscopy) in 56% yield (Table). The isomer ratio was calculated from the integration of the resonances at δ 6.08 [d, 3 H of (4)], 5.4—5.3 [m, 2- and 3-H of (2) and (3)], 3.65 [s, CO_2Me of (2) overlapped with the signal for 1-H of (4)], and 3.56 [s, CO_2Me of (3)] (see below for full spectral information of the pure isomers).

The mixture of the ester complexes (6.35 g, 23 mmol) was stirred magnetically with aqueous sodium hydroxide (20%, 200 ml) in methanol (300 ml) at 5—10 °C for 2 h.[16] The crude mixture (6.0 g, 90%) of carboxy-complexes was fractionally recrystallized (from $CHCl_3$ and hexane), with *slow* cooling, to give an initial crop of pale yellow crystals (1.75 g, 28%), of *tricarbonyl-*(η^4*-5β-methoxycarbonylcyclohexa-*1,3*-diene)iron* (2). An analytical sample was obtained by recrystallization from $CHCl_3$–hexane, m.p. 116—119 °C (decomp.); $\nu_{max.}$ ($CHCl_3$) 3 200—2 480br (CO_2H), 2 040, 1 955, and 1 700 cm^{-1}; δ 9.3br (s, CO_2H), 5.30 (2-H, m, 2- and 3-H), 3.30 (2 H, m, 1- and 4-H), 2.57 (1 H, m, $J_{5,6\alpha}$ 8, $J_{5,6\beta}$ 4—6 Hz, 5-H), 2.24 (2 H, m,* $J_{6\beta,6\alpha}$ 15 $J_{6\beta,4}$ 4 Hz, 6β-H), and 1.89 (1 H, m,* $J_{6\alpha,4}$ 3 Hz, 6α-H); *m/z* 264 (*M*), 236 (*M* − CO), 208 (*M* − 2CO), and 180 (*M* − 3CO) (Found: C, 45.3; H, 3.6. $C_{10}H_8FeO_5$ requires C, 45.5; H, 3.1%).

The mother liquor was concentrated and cooled (4 °C) to give a second crop (1.78 g, 28%) of yellow crystals. ^1H N.m.r. spectroscopy indicated the presence of both 5α- and 5β-carboxy-complexes in a ratio of 3 : 1. Efficient fractional sublimation of this solid gave two crystalline solids identified as *tricarbonyl-*(η^4*-5α-carboxycyclohexa-*1,3*-diene)iron* (3) (m.p. 91—93 °C, 90—100 °C/0.05 mmHg) and the 5β-carboxy-complex (110 °C/0.05 mmHg), the former being more volatile. The 5α-carboxy-complex displayed the following spectral characteristics: $\nu_{max.}$ ($CHCl_3$) 3 200—2 480br (CO_2H), 2 040, 1 960, and 1 695 cm^{-1}; δ($CDCl_3$) 9.8br (s, CO_2H), 5.4 (2 H, m, 2- and 3-H), 3.12 (2 H, m, 1- and 4-H), 2.92 (1 H, m, 5-H), 2.09 (1 H, m,* 6β-H), and 1.87 (1 H, m,* 6α-H); *m/z* 264 (*M*), 236 (*M* − CO), 208 (*M* − 2CO), and 180 (*M* − 3CO) (Found: C, 45.5; H, 3.3%. $C_{10}H_8FeO_5$ requires C, 45.5; H, 3.1%).

A third crop of crystals (1.36 g, 21%) obtained from recrystallization consisted of 5β, 2- and 5α-carboxy-complexes in a ratio of 7 : 4 : 2 as indicated by ^1H n.m.r. spectroscopy. The isomer ratio was calculated from the resonances at δ 6.16 (d, 3-H of 2-carboxy-complex), 5.4—5.3 (m, 2- and 3-H of 5β- and 5α-carboxy-complexes), 3.76 (d, 1-H of 2-carboxy-complex), 2.92 (m, 5-H of 5α-carboxy-complex), and 2.57 (m, 5-H of 5β-carboxy-complex). The

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* CH_2 (β)-splitting pattern (ref. 1).

spectral characteristics of the 2-carboxy-complex and the corresponding methyl ester have been reported elsewhere.[4]

Methylation (Me_2SO_4–K_2CO_3–Me_2CO) of the 5α-carboxy-complex (1.1 g, 4.2 mmol) gave the *5α-methyl ester* (3) as a yellow oil (b.p. 96—98 °C/0.7 mmHg; 1.16 g, 99%); $\nu_{max.}$ (film) 2 050, 1 970, and 1 735 cm^{-1}; δ($CDCl_3$) 5.4 (2 H, m, 2- and 3-H), 3.56 (3 H, s, CO_2Me), 3.1 (2 H, m, 1- and 4-H), 2.9 (1 H, m, 5-H), 2.09 (1 H, m,* 6β-H), 1.187 (1 H, m,* 6α-H). The complex (3) was unaffected by $Ph_3C^+PF_6^-$.

The *5β-methyl ester* (2) was similarly obtained in 75% yield by methylation of the 5β-carboxy-complex; $\nu_{max.}$ (film) 2 050, 1 960, and 1 730 cm^{-1}; δ 5.28 (2 H, m, 2- and 3-H), 3.65 (3 H, s, CO_2Me), 3.28 (2 H, m, 1- and 4-H), 2.48 (1 H, m, $J_{5.6\alpha}$ 8, $J_{5.6\beta}$ 4—6 Hz, 5-H), 2.24 (1 H, m, $J_{6\beta.6\alpha}$ 15 Hz, 6β-H), and 1.89 (1 H, m, $J_{6\alpha.4}$ 4 Hz, 6α-H); *m/z* 278 (*M*), 250 (*M* — CO), 222 (*M* — 2CO), and 194 (*M* — 3CO). Treatment of the ester (2) with $Ph_3C^+PF_6^-$ in acetonitrile afforded tricarbonyl-(η^5-6β-methoxycarbonylcyclohexadienylium)iron hexafluorophosphate.[1]

Application of Complexation Conditions to Compounds (2), (3) *and* (4).—Each compound (100 mg), dissolved in di-n-butyl ether (5 ml), was heated with pentacarbonyliron (0.1 ml) for 20 h under reflux. The crude products, 90% yield from compound (2), 70% from compound (3), and 75% from compound (4), displayed ^1H n.m.r. spectra identical with the starting ester complex. A small amount of aromatic material was noted (^1H n.m.r. spectroscopy) in each case.

Reaction of Methyl Cyclohexa-2,5-*dienecarboxylate* (1) *with Pentacarbonyliron under Different Conditions*.—The reaction conditions and yields are given in the Table. The thermal conditions were applied for large amounts of the diene precursor (5—10 g) and photochemical conditions for small amounts (2 g, 500 ml of solvent).

Reaction of p-*Bromophenacyl Cyclohexa*-2,5-*dienecarboxylate* (5) *with Pentacarbonyliron*.—A mixture of potassium cyclohexa-2,5-dienecarboxylate (7.0 g, 43.2 mmol), *p*-bromophenacyl bromide (6.0 g, 21.6 mmol), and 18-crown-6 ether (1.32 g, 5 mmol, 0.05M) in acetonitrile was stirred magnetically under reflux for 1 h.[11] The mixture was cooled, filtered, and concentrated. Removal of 18-crown-6 by filtration through a column of silica in benzene gave, after recrystallisation from EtOH–H_2O, the diene precursor (5) as white crystals (5.0 g, 70%), m.p. 73—75 °C; $\nu_{max.}$ (Nujol) 1 725s (phenacyl CO), 1 705s ester CO), 1 640w, and 1 585w cm^{-1}; δ($CDCl_3$) 7.69 (4 H, AB q, Ar-H), 5.87br (4 H, s, diene H), 5.27 (2 H, s, CO_2CH_2CO), 3.93 (1 H, t, $J_{1.4}$ 8 Hz, 1-H), and 2.63.

Complexation of the diene ester (5) with $Fe(CO)_5$ under thermal conditions afforded a dark brown sticky residue which was distilled (150 °C/0.001 mmHg) to give the unstable complex *tricarbonyl*-(η^4-5β-p-*bromophenacylcyclohexa*-1,3-*diene*)*iron* (6) in very low yield (*ca.* 5%), contaminated (^1H n.m.r. spectroscopy) with small amounts of *p*-bromophenacylbenzoate (comparison with authentic sample) and *p*-bromoacetophenone (authentic sample). The instability and small amounts of material available prevented separation of these impurities and acceptable combustion analysis could not be obtained; however, the structure of the major component was confirmed by conversion (see below) into known compounds. The spectral characteristics of compound (6) are: $\nu_{max.}$ ($CHCl_3$) 2 045, 1 970, 1 735, and 1 700 cm^{-1}; δ($CDCl_3$) 7.3 (m, Ar-H), 5.24 (m, 2- and 3-H, and CO_2-CH_2-CO), 3.2 (m, 1- and 4-H), 2.62 (m, 5-H), 2.23 (m,† 6β-H), and 1.88 (m,† 6a-H); *m/z* 406 and 404 (*M* — 2CO), 378 and 376 (*M* — 3CO), and 320 and 318 (*M* — 3 × CO-Fe-2H). Removal of the *p*-bromophenacyl group with Zn-AcOH[12] at room temperature for 1 h gave the 5β-carboxy-complex (^1H n.m.r. spectroscopy), methylation (Me_2SO_4) of which afforded the 5β-methoxycarbonyl complex (2) (^1H n.m.r. and i.r. spectroscopy, t.l.c.) identical with authentic sample.

Reaction of Methyl 3,5-*Dimethoxycyclohexa*-2,5-*dienecarboxylate* (7) *with Pentacarbonyliron*.—The diene precursor (7) was prepared in 71% yield from 3,5-dimethoxybenzoic acid by methylation (Me_2SO_4) of the Birch reduction product;[20] $\nu_{max.}$ (film) 1 730, 1 695, 1 660, and 1 595 cm^{-1}; δ($CDCl_3$) 4.78 (2 H, d, $J_{1.2}$, $J_{1.6}$ 3.5 Hz, 2- and 6-H), 3.93 (1 H, dt, $J_{1.4}$ 7.5 Hz, 6-H), 3.70 (3 H, s, CO_2Me), 3.60 (6 H, s, 2 × OMe), and 2.78 (2 H, d, 4-H).

Complexation of the crude ester (7) (500 mg, 2.53 mmol) under thermal conditions for 40 h afforded a viscous brownish oil. Passage through a column of silica gel H (type 60), using light petroleum and Et_2O (10%) as the eluant, gave a homogeneous (t.l.c.), viscous yellow oil (550 mg, 64%) which was identified as *tricarbonyl*-(η^4-1,3-*dimethoxy*-5α-*methoxycarbonylcyclohexa*-1,3-*diene*)*iron* (8); $\nu_{max.}$ (film) 2 035, 1 965, and 1 725 cm^{-1}; δ($CDCl_3$) 5.39 (1 H, d, $J_{2.4}$ 2 Hz, 2-H), 3.58 (6 H, s, 3-OMe and CO_2Me), 3.36 (3 H, s, 1-OMe), 3.17 (1 H, dd, $J_{4.5}$ 4 Hz, 4-H), 2.90 (1 H, m, 5-H), 2.42 (1 H, dd, $J_{6\beta,6\alpha}$ 14, $J_{6\beta,5}$ 11 Hz, 6β-H), and 1.87 (1 H, dd, $J_{6\alpha.5}$ 5 Hz, 6α-H); *m/z* 338 (*M*), 310 (*M* — CO), 282 (*M* — 2CO), and 254 (*M* — 3CO). The ester (8) did not react with $Ph_3C^+PF_6^-$.

Reaction of Methyl 3,5-*Dimethoxy*-1-*methylcyclohexa*-2,5-*dienecarboxylate* (9).—Reductive methylation of 3,5-dimethoxybenzoic acid was carried out according to the procedure of Birch and his co-workers[15] to yield 3,5-dimethoxy-1-methylcyclohexa-2,5-diene-1-carboxylic acid as crystals, m.p. 97—98 °C (diethyl ether–light petroleum) (lit.,[15a] 97—102 °C). Esterification of the acid with Me_2SO_4 gave the diene ester (9) as a solid, m.p. 49—51 °C; δ($CDCl_3$) 4.62 (2 H, s, 2- and 6-H), 3.57 (3 H, s, CO_2Me), 3.52 (6 H, d, OMe), 2.63 (2 H, s, 4-H), and 1.3 (3 H, s, Me).

The complexation of this ester (0.25 g, 1.18 mol) under thermal conditions afforded, after passage through Celite, a yellow oil (0.25 g) which solidified on standing. Chromatography over silica (hexane–diethyl ether, 1 : 1) gave a single yellow band (0.24 g, 58%) which appeared from ^1H n.m.r. spectroscopy and t.l.c. to be a mixture of two complexes in the ratio of 1 : 1. Chromatography over silica gel H (type 60) using a mixture of hexane and diethyl ether (2 : 1) gave two distinct bands which were collected and identified.

The first compound (0.12 g) eluted from the column was identified as *tricarbonyl*-(η^4-1,3-*dimethoxy*-6β-*methoxycarbonyl*-6α-*methylcyclohexa*-1,3-*diene*)*iron* (10), m.p. 98—99 °C (light petroleum); $\nu_{max.}$ ($CHCl_3$) 2 045, 1 970, and 1 730 cm^{-1}; δ($CDCl_3$) 5.27 (1 H, d, $J_{2.4}$ 2.5 Hz, 2-H), 3.76 (3 H, s, CO_2Me), 3.63 (3 H, s, 3-OMe), 3.49 (1 H, d, 4-H), 3.44 (3 H, s, 1-OMe), 3.07 (1 H, d, $J_{6\alpha.6\beta}$ 15 Hz, 6β-H), 1.51 (1 H, d, 6α-H), and 1.36 (3 H, s, Me); *m/z* 352 (*M*), 324 (*M* — CO), 296 (*M* — 2CO), and 268 (*M* — 3CO); a single-crystal *X*-ray analysis[21] of this compound confirmed the stereochemistry at C-5.

The compound (0.12 g) less mobile in the column was identified as *tricarbonyl*-(η^4-1,3-*dimethoxy*-6α-*methoxycarbonyl*-6β-*methylcyclohexa*-1,3-*diene*)*iron* (11); $\nu_{max.}$ ($CHCl_3$) 2 045, 1 970, and 1 720 cm^{-1}; δ($CDCl_3$) 5.27 (1 H, d, $J_{2.4}$

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* CH_2 (α)-splitting pattern (ref. 1).

† CH_2 (β)-splitting pattern (ref. 1).

2.5 Hz, 2-H), 3.63, 3.62 (6 H, s, s, CO_2Me and 3-OMe), 3.42 (3 H, s, 1-OMe), 3.04 (1 H, d, 4-H), and 2.46—1.97 (2 H, AB quartet, 6-H); *m/z* 352 (*M*), 324 (*M* − CO), 296 (*M* − 2CO), and 268 (*M* − 3CO).

Reaction of Methyl 2-*Methoxycyclohexa*-2,5-*dienecarboxylate* (12) *with Pentacarbonyliron.*—Lithium–ammonia reduction of methyl 2-methoxybenzoate (10 g, 60 mmol) in the presence of water[22] (1.62 g, 90 mmol) gave the diene precursor (12)[3] (9.8 g, 97%). The complexation of the crude ester (9.8 g, 58 mmol) under thermal conditions afforded, after subsequent passage through a column of silica gel as above, a viscous yellow oil (10 g, 55%) comprising a mixture of three isomeric complexes (t.l.c., ^1H n.m.r. and m.s. spectra):[4] tricarbonyl-(η^4-1-methoxy-6β-methoxycarbonylcyclohexa-1,3-diene)iron (13), tricarbonyl-(η^4-1-methoxy-6α-methoxycarbonylcyclohexa-1,3-diene)iron (14), and tricarbonyl-(η^4-1-methoxy-2-methoxycarbonylcyclohexa-1,3-diene)iron (15). The isomer ratio of (13) : (14) : (15) was calculated to be 5 : 6 : 9 from the integration of the resonances at δ 5.41 [2-H of (14)], 5.28 [2-H of (13)], 5.10 [3-H of (14)], 4.87 [3-H of (13)], and 4.56 [3-H of (15)].

Reaction of Dimethyl Cyclohexa-2,5-*diene*-1,2-*dicarboxylate* (16) *with Pentacarbonyliron.*—*trans*-Cyclohexa-3,5-diene-1,2-dicarboxylic acid, prepared by reduction[14, 23] of benzene-1,2-dicarboxylic acid with Na–Hg in AcOH–AcONa, was isomerised[14] in water to obtain cyclohexa-2,5-diene-1,2-dicarboxylic acid which, upon methylation with BF_3–Et_2O–MeOH, gave the diene precursor (16) as an oil, b.p. 90—91 °C/0.4 mmHg, in 76% yield; $\nu_{max.}$ (film) 1 740s, 1 715s, 1 680, and 1 650 cm^{-1}; δ(CD_3Cl) 7.12 (1 H, t with fine splitting, $J_{3.4}$ 3.5, $J_{1.3}$ 1, $J_{3.5}$ 6.5 Hz, 3-H), 5.82 (2 H, m, 5- and 6-H), 4.08 (1 H, t with fine splitting, $J_{1.4}$ 7.5, $J_{1.6}$ 1 Hz, 1-H), 3.71 (3 H, s, 2-CO_2Me), 3.66 (3 H, s, 1-CO_2Me), and 2.90 (2 H, dd with fine splitting, 4-H); δ(^{13}C, CCl_4) 171.16 (s, *C*O_2Me), 165.70 (s, *C*O_2Me), 137.52 (d, $^1J_{CH}$ 162.1 Hz, 3-C), 125.06 (d of multiplets, $^1J_{CH}$ 161.1, $^2J_{CH}$ 5.9, 7.8 Hz, 6-C), 122.72 (d of multiplets, $^1J_{CH}$ 164.1 Hz, $^2J_{CH}$ 5.9, 7.8 Hz, 5-C), 51.8 (q, $^1J_{CH}$ 146.5 Hz, OMe), 51.42 (q, $^1J_{CH}$ 146.5 Hz, OMe), 42.20 (d, $^1J_{CH}$ 131.8 Hz, 1-C), and 27.14 p.p.m. (t, $^1J_{CH}$ 129.9 Hz, 4-C).

Complexation of the diene ester (16) (1.23 g, 6.28 mmol) with $Fe(CO)_5$ (5 ml) under thermal conditions gave a mixture of three (t.l.c.) isomeric complexes (1.56 g, 74%). The yield varied to 93% in different runs. The components of the mixture were separated by t.l.c. (benzene–acetonitrile 5% v : v, *ca.* 100 mg on each plate).

The most mobile (t.l.c.) compound was obtained as pale yellow needles and was identified as *tricarbonyl* (η^4-5α,6β-*dimethoxycarbonylcyclohexa*-1,3-*diene*)*iron* (19), m.p. 62—63 °C (from light petroleum); $\nu_{max.}$ ($CHCl_3$) 2 055, 1 989, and 1 727 cm^{-1}; δ($CDCl_3$) 5.38 (2 H, m, 2- and 3-H), 3.70 (3 H, s, 6β-CO_2Me), 3.62 (3 H, s, 5α-CO_2Me), 3.40 (1 H, dd, $J_{5.6}$ 4.5, $J_{5.4}$ 3.6 Hz, 5-H), 3.32 (1 H, dt, $J_{1.2}$ 6.5, $J_{1.6}$ 2.0, $J_{1.3}$ 1.7 Hz, 1-H), 3.17 (1 H, ddd, $J_{4.3}$ 6.5, $J_{2.4}$ 1.7 Hz, 4-H), and 2.97 (1 H, dd, 6-H); *m/z* 336 (*M*), 308 (*M* − CO), 280 (*M* − 2CO), and 252 (*M* − 3CO) (Found: C, 47.1; H, 3.7, $C_{13}H_{12}FeO_7$ requires C, 46.5; H, 3.6%). The determination of the coupling constants and the assignment of resonances in the ^1H n.m.r. spectra were made by application of double resonance techniques in the presence of $Eu(fod\text{-}d_9)_3$, *ca.* 1.1 × 10^{-1} mol l^{-1}.

The second band (t.l.c.) gave *tricarbonyl*-(η^4-1,6α-*dimethoxycarbonylcyclohexa*-1,3-*diene*)*iron* (18) as yellow crystals, m.p. 55—56 °C (from light petroleum); $\nu_{max.}$ ($CHCl_3$) 2 058, 1 990, 1 722, and 1 702 cm^{-1}; δ($CDCl_3$) 6.23 (1 H, dt, $J_{2.3}$ 4.5, $J_{2.4}$, $J_{2.6}$ 1.0 Hz, 2-H), 5.43 (1 H, ddd, $J_{3,4}$ = 7.5, $J_{3.5\alpha}$ 0.9 Hz, 3-H), 3.66 (3 H, s, 1-CO_2Me), 3.57 (3 H, s, 6α-CO_2Me), 3.43 (1 H, ddd, $J_{6.5\beta}$ 12.0, $J_{6.5\alpha}$ 3.7 Hz, 6β-H), 3.21 (1 H, m, $J_{4.5\alpha}$ 2.8, $J_{4.5\beta}$ 3.5 Hz, 4-H), 2.38 (1 H, m, $J_{5\beta,5\alpha}$ 15.5 Hz, 5β-H), and 1.81 (1 H, m, 5α-H); *m/z* 336 (*M*), 308 (*M* − CO), 280 (*M* − 2CO), and 252 (*M* − 3CO) (Found: C, 46.4; H, 3.6. $C_{13}H_{12}FeO_7$ requires C, 46.5; H, 3.6%).

The third t.l.c. band gave tricarbonyl-(η^4-1,6β-dimethoxycarbonylcyclohexa-1,3-diene)iron (17) as yellow crystals, m.p. 92—93 °C (from light petroleum); $\nu_{max.}$ ($CHCl_3$) 2 060, 1 988, 1 722, and 1 697 cm^{-1}; 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_2Me), 3.63 (3 H, s, 6β-CO_2Me), 3.41 (1 H, m, $J_{4.5}$ 3 Hz, 4-H), 2.35 (1 H, dd, $J_{5.6\alpha}$ 8, $J_{6.5\beta}$ 6 Hz, 6α-H), and 2.26—1.5 (2 H, m, 5-H); *m/z* 336 (*M*), 308 (*M* − CO), 280 (*M* − 2CO), and 252 (*M* − 3CO) (Found: C, 46.8; H, 3.9. $C_{13}H_{12}FeO_7$ requires C, 46.5; H, 3.6%).

The structures of compounds (17) and (18) were confirmed by *X*-ray analysis.[21] The isomer ratio of the above compounds prior to t.l.c. was estimated from ^1H n.m.r. spectroscopy to the (17) : (18) : (19) = 1 : 3 : 1. The integration of the resonances at δ 6.23 [2-H of (18)], 5.91 [2-H of (17)], and 5.38 [2- and 3-H of (19)] was considered for this calculation.

The mixture of the three isomeric complexes (t.l.c.), produced in <30% yield upon boiling the diene and $Fe(CO)_5$ in xylene under reflux for 18 h, was found ot be (17), (18), and (19) in the ratio 4 : 7 : 4 (^1H n.m.r. spectroscopy).

Reaction of Blocked Cyclohexa-1,4-*diene Esters with Pentacarbonyliron.*[5]—*Tricarbonyl*(η^4-5β-*methoxycarbonyl*-5α-*methylcyclohexa*-1,3-*diene*)*iron* (29). Reductive methylation[15] of benzoic acid, followed by methylation (Me_2SO_4), yielded methyl 1-methylcyclohexa-2,5-dienecarboxylate (24); δ($CDCl_3$) 5.8 (4 H, s, diene H), 3.67 (3 H, s, CO_2Me), 2.64 (2 H, s, 4-H), and 1.31 (3 H, s, Me).

The complexation of the ester (24) (2 g, 13 mmol) under thermal conditions gave a viscous yellow oil (1.65 g). The ^1H n.m.r. spectrum of the product indicated the presence of unchanged diene (30%) and the complex ester (29) (35%). Starting material was only partially removed by passage through a column of silica H (type 60), using benzene and acetonitrile (5% *v/v*). Separation was achieved by selective hydrolysis of the unchanged starting material. The mixture was dissolved in methanol and stirred with aqueous NaOH (excess) at 5—10 °C for 2 h. The complex ester, extracted from the mixture with light petroleum, was found to be completely free of the starting diene. The overall yield of the complex ester (29) was 44% (based on the diene reacted in the complexation process) which was obtained as *yellow crystals*, m.p. 53—54 °C (from light petroleum); $\nu_{max.}$ ($CHCl_3$) 2 045, 1 975, and 1 715 cm^{-1}; δ($CDCl_3$) 5.30 (2 H, m, 2- and 3-H), 3.66 (3 H, s, CO_2Me), 3.37 (1 H, dd, $J_{3.4}$ 6 Hz, $J_{2.4}$ 2 Hz, 4-H), 3.06 (1 H, m, 1-H), 2.58 (1 H, dd, $J_{6\beta.6\alpha}$ 16, $J_{6\beta.1}$ 3.5 Hz, 6β-H), 1.52 (1 H, dd, $J_{6\alpha.1}$ 2.7 Hz, 6α-H), and 1.20 (3 H, s, Me); *m/z* 292 (*M*), 264 (*M* − CO), 236 (*M* − 2CO), and 208 (*M* − 3CO) (Found: C, 50.0; H, 4.2. $C_{12}H_{12}FeO_5$ requires C, 49.4; H, 4.1%).

Tricarbonyl-(η^4-5α-*benzyl*-5β-*methoxycarbonylcyclohexa*-1,3-*diene*)*iron* (30). Reductive alkylation[15] of benzoic acid with benzyl bromide[24] gave 1-benzylcyclohexa-2,5-dienecarboxylic acid (92% yield), methylation (Me_2SO_4) of which afforded methyl 1-benzylcyclohexa-2,5-dienecarboxylate (25) in 98% yield as an oil; $\nu_{max.}$ (film) 1 725s, 1 635w, and 1 600w; δ 7.15 (5 H, s, Ar-H), 5.80 (4 H, s, diene H), 3.61 (3 H, s, CO_2Me), 2.98 (2 H, s, CH_2Ph), and 2.43 (2 H, narrow m, 4-H).

Complexation of the crude ester (25) (1.5 g, 6.9 mmol) under thermal conditions for 40 h gave a yellow solid (2.51 g, 98%), identified as the complex ester (30), which was recrystallized to give yellow crystals, m.p. 61—62 °C (from light petroleum); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, and 1 730 cm^{-1}; δ($CDCl_3$) 7.0 (5 H, m, ArH), 5.27 (2 H, m, 2- and 3-H), 3.63 (3 H, s, CO_2Me), 3.30 (1 H, dd, $J_{3.4}$ 6, $J_{2.4}$ 2 Hz, 4 H), 3.03 (1 H, m, 1-H), 2.77 (2 H, s, CH_2Ph), 2.53 (1 H, dd, $J_{6\beta,6\alpha}$ 16, $J_{6\beta,1}$ 4 Hz, 6β H), and 1.77 (1 H, dd, $J_{6\alpha,1}$ 2.7 Hz, 6α-H); *m/z* 368 (*M*), 340 (*M* — CO), 312 (*M* — 2CO), and 284 (*M* — 3CO) (Found: C, 58.6; H, 4.4. $C_{18}H_{16}FeO_5$ requires C, 58.7; H, 4.4%).

Tricarbonyl-[η^4*-5α-(3,5-dimethoxy)benzyl-5β-methoxycarbonylcyclohexa-*1,3*-diene*]*iron* (31). Methyl 1-(3,5-dimethoxy)benzylcyclohexa-2,5-dienecarboxylate (26) (1.5 g, 5.2 mmol), prepared by the following sequence: the product of reductive alkylation (3,5-dimethoxybenzyl bromide [25]) of benzoic acid and methylation (Me_2SO_4) was treated with $Fe(CO)_5$ (3.0 ml) under thermal conditions for 40 h to give the complex ester (31) as yellow crystals (2.19 g, 98%), m.p. 84—85 °C (from light petroleum); $\nu_{max.}$ ($CHCl_3$) 2 040, 1 985, 1 715, 1 600, and 1 595 cm^{-1}; δ($CDCl_3$) 6.30 (1 H, t, $J_{2',4'}$, $J_{4',6'}$ 2 Hz, 4′-H), 6.15 (2 H, d, 2′- and 6′-H), 5.31 (2 H, m, 2- and 3-H), 3.70 (6 H, s, 2 × OMe), 3.63 (3 H, s, CO_2Me), 3.28 (1 H, dd, $J_{3.4}$ 6, $J_{2.4}$ 2 Hz, 4-H), 3.05 (1 H, m, 1-H), 2.69 (2 H. AB q, CH_2-Ar), 2.49 (1 H, dd, $J_{6\beta,6\alpha}$ 16.2, $J_{6\beta,1}$ 3.7 Hz, 6β-H), and 1.78 (1 H, dd, $J_{6\alpha,1}$ 3 Hz, 6α-H); *m/z* 428 (*M*), 400 (*M* — CO), 372 (*M* — 2CO), and 344 (*M* — 3CO) (Found: C, 55.9; H, 4.7; $C_{12}H_{20}FeO_7$ requires C, 56.1; H, 4.7%).

Tricarbonyl-(η^4*-6β-methoxycarbonyl-*1,6α*-dimethylcyclohexa-*1,3*-diene*)*iron* (32). Methyl 1,2-dimethylcyclohexa-2,5-dienecarboxylate (27) was prepared in 81% yield by reductive methylation of *o*-methylbenzoic acid,[15] followed by methylation of the resulting dihydro-acid; compound (27) gave $\nu_{max.}$ (film) 1 725 cm^{-1}; δ($CDCl_3$) 5.9—5.4 (3 H, m, 3-, 5-, and 6-H), 3.67 (3 H, s, CO_2Me), 2.71 (2 H, m, 4-H), 1.68 (3 H, m, coupled to diene and 4-H, 2-Me), and 1.37 (3 H, s, 1-Me).

Complexation of the diene (27) (4.0 g, 26.3 mmol) with $Fe(CO)_5$ under thermal conditions for 40 h gave a viscous oil (6.74 g, 88%), homogeneous in t.l.c. The compound was identified as the *complex* (32); $\nu_{max.}$ (film) 2 045, 1 980, and 1 730 cm^{-1}; δ($CDCl_3$) 5.2 (2 H, m, 2- and 3-H), 3.70 (3 H, s, CO_2Me), 3.07 (1 H, m, 4-H), 2.57 (1 H, dd, $J_{5\alpha,5\beta}$ 16, $J_{4,5\beta}$ 3—4 Hz, 5β-H), 1.72 (1 H, dd, $J_{4,5\alpha}$ 3 Hz, 5α-H), 1.47 (3 H, s, 1-Me), and 1.20 (3 H, s, 6α-Me); *m/z* 306 (*M*), 278 (*M* — CO), 250 (*M* — 2CO), and 222 (*M* — 3CO).

Tricarbonyl-(η^4*-6β-methoxycarbonyl-*2,6α*-dimethylcyclohexa-*1,3*-diene*)*iron* (33). Methyl 1,3-dimethylcyclohexa-2,5-dienecarboxylate (28) was prepared in 86% yield from 3-methylbenzoic acid as above and had $\nu_{max.}$ (film) 1 735 cm^{-1}; δ($CDCl_3$) 5.78br (2 H, s, 5- and 6-H), 5.5 (1 H, narrow m, 2-H), 3.67 (3 H, s, CO_2Me), 2.57br (2 H, s, 4-H), 1.74br (3 H, s, 3-Me), and 1.33 (3 H, s, 1-Me).

Complexation of the diene (28) (4.0 g, 26.3 mmol) with $Fe(CO)_5$ under thermal conditions for 40 h afforded a viscous yellow oil (5.80 g, 76%), homogeneous in t.l.c. The product was identified as the *complex* (33); $\nu_{max.}$ (film) 2 050, 1 980, and 1 735 cm^{-1}; δ($CDCl_3$) 5.28 (1 H, d, *J* 6 Hz, 3-H), 3.73 (3 H, s, CO_2Me), 3.38 (1 H, d, *J* 1.5 Hz, 1-H), 2.92 (1 H, m, 4-H), 2.57 (1 H, dd, $J_{5\alpha,5\beta}$ 16, $J_{5\beta,4}$ 4 Hz, 5β-H), 2.15 (3 H, s, 2-Me), 1.5 (1 H, dd, $J_{5\alpha,4}$ 3 Hz, 5-H), and 1.20 (3 H, s, 6α-Me); *m/z* 306 (*M*), 278 (*M* — CO), 250 (*M* — 2CO), and 222 (*M* — 3CO).

Complexation of cis*-Cyclohexa-*3,5*-diene-*1,2*-dicarboxylic Anhydride* (34).—The diene precursor (34) was prepared by the reaction of *trans*-cyclohexa-3,5-diene-1,2-dicarboxylic acid with acetic anhydride [17] and gave m.p. 108—110 °C (lit.,[17] 108—109.5 °C); $\nu_{max.}$ (Nujol) 1 860 and 1 785 cm^{-1}; δ(C_6D_6) 5.35 (4 H, narrow m, diene H) and 2.82 (2 H, s, methine H).

The *cis*-anhydride (34) (1.0 g, 6.7 mmol) was treated with $Fe_2(CO)_9$ (3.64 g, 10 mmol) in butan-2-one (20 ml) under reflux for 4.5 h. The crude residue obtained after normal work-up [10] was sublimed at 96—100 °C/0.001 mmHg to give yellow crystals (170 mg, 10%). The product was identified as a 2 : 1 mixture of *tricarbonyl-*(η^4*-cyclohexa-*3,5*-diene-*1β,2β*-dicarboxylic anhydride*)*iron* (35) and *tricarbonyl-*(η^4*-cyclohexa-*3,5*-diene-*1α,2α*-dicarboxylic anhydride*)*iron* (36) from the following spectral properties: $\nu_{max.}$ (Nujol) 2 065, 2 000, 1 860, and 1 787 cm^{-1}; δ($CDCl_3$) 5.56 [dd, 2- and 3-H of (35)], 3.48 [narrow m, 5- and 6-H of (36)], 3.24 [m, 1- and 4-H of (35) and (36)], and 2.98 [m, 5- and 6-H of (35) and (36)]; *m/z* 290 (*M*), 262 (*M* — CO), 234 (*M* — 2CO), and 206 (*M* — 3CO). The isomer ratio was deduced from the integration of resonances at δ 5.56 and 5.33.

Physical selection of the deeper yellow crystals in the mixture and subsequent recrystallization from $CHCl_3$ and light petroleum gave yellow crystals, which had physical properties consistent with the 5α,6α-anhydride structure (36)], m.p. 162—163 °C; $\nu_{max.}$ ($CHCl_3$) 2 060, 1 995, 1 858, and 1 778 cm^{-1}; δ($CDCl_3$, HA 100 instrument) 5.62 (2 H, dd, 2- and 3 H), 3.51 (2 H, t, $J_{5,4}$, $J_{5,1}$ 4.5 Hz, 5- and 6-H), and 3.23 (2 H, m, 1- and 4-H); (Found: *M*, 290.9520. Calc. for $C_{11}H_6FeO_6$: 290.9514).

Complexation of the *cis*-anhydride (34) (500 mg, 3.3 mmol) with $Fe(CO)_5$ (1.7 ml) in diethyl ether (500 ml) under photochemical conditions for 4—5 h gave a brownish sticky residue which, after sublimation at 96—100 °C/0.001 mmHg, afforded pale yellow crystals (30 mg, >5%). The product was identified (^{1}H n.m.r., i.r., and mass spectra) as a mixture of the 5β,6β-anhydride (35) and 5α,6α-anhydride (36) complexes in a ratio of 4 : 1.

Reaction of cis*-Dimethyl Cyclohexa-*3,5*-diene-*1,2*-dicarboxylate* (37) *with Pentacarbonyliron.*—Esterification of *cis*-cyclohexa-3,5-diene-1,2-anhydride (3.0 g, 22.4 mmol) with BF_3–Et_2O–MeOH [18] gave the diene precursor (37) as an oil (2.9 g, 75%); $\nu_{max.}$ ($CHCl_3$) 1 748s, 1 610w, and 1 590w cm^{-1}; δ 5.94 (4 H, m, diene H) and 3.6 (8 H, s, 2 × CO_2Me and methine H).

The *cis*-diester (37) (1.0 g, 5.1 mmol) and $Fe(CO)_3$ (2.0 ml) in Et_2O (1 l) were mixed under photochemical conditions for 4.5 h. The crude product (1.85 g) obtained after normal work-up was sublimed at reduced pressure to yield a yellow solid (1.43 g, 83%). The product, composed of two compounds (t.l.c.) was separated by fraction recrystallization from light petroleum.

The first crop afforded the major component as moderately unstable buff crystals, m.p. 106—107 °C, and had properties consistent with *tricarbonyl-*(η^4*-5β,6β-dimethoxycarbonylcyclohexa-*1,3*-diene*)*iron* (38); $\nu_{max.}$ ($CHCl_3$) 2 055, 1 985, and 1 730 cm^{-1}; δ($CDCl_3$) 5.26 (2 H, m, 2- and 3-H), 3.63 (6 H, s, 2 × CO_2Me), 3.22 (2 H, m, 1- and 4-H), and 2.92 (2 H, s, 5- and 6-H); *m/z* 336 (*M*), 308 (*M* — CO), 280 ($M - 2CO$), and 252 ($M - 3CO$) (Found: C, 46.4; H, 3.8. $C_{13}H_{12}FeO_7$ requires C, 46.5; H, 3.6%).

The second crop gave stable yellow prisms, m.p. 97—98 °C, which had properties consistent with *tricarbonyl-*(η^4-*5α,6α-dimethoxycarbonylcyclohexa-*1,3-*diene*)*iron* (39); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 980, and 1 730 cm^{-1}; δ($CDCl_3$) 5.50 (2 H, m, 2- and 3-H), 3.55 (6 H, s, 2 × CO_2Me), 3.26 (2 H, narrow m, 5- and 6-H), and 3.10 (2 H, m, 1- and 4-H); *m/z* 336 (*M*), 308 ($M - CO$), 280 ($M - 2CO$), and 252 ($M - 3CO$) (Found: C, 46.8; H, 3.7. $C_{13}H_{12}FeO_7$ requires C, 46.5; H, 3.6%).

The isomer ratio of (38) and (39) prior to separation was calculated to be 2 : 1 from the integration of resonances at δ 5.50, 5.26, 3.63, 3.55, 3.10, and 2.92.

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