# Organoiron Complexes in Organic Synthesis. Part 3.[1] An Approach to the Synthesis of Spirocyclic Compounds from Tricarbonyldieneiron Complex Intermediates

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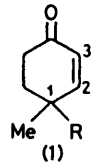
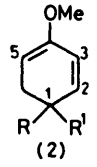
Synthesis of methyl 8-methoxy-2-oxospiro[4.5]deca-6,8-diene-3-carboxylate (14) in eight steps from *p*-methoxycinnamic acid is described. The method involves cyclisation of the 1,1-disubstituted-cyclohexa-2,4-diene (2d) which is readily obtained from tricarbonyl[η-1—5-1-(3'-methoxycarbonylpropyl)-4-methoxycyclohexa-2,4-dienylium]iron hexafluorophosphate (3b). A similar series of reactions starting from 4-(*p*-methoxyphenyl)butyric acid leads ultimately to methyl 3-methoxy-8-oxospiro[5.5]undeca-1,3-diene-9-carboxylate (16). In the course of investigating model systems the trichodermin intermediate (1c) has also been synthesised.

BECAUSE of its presence in a number of naturally occurring sesquiterpenes,[2] synthesis of the spiro[4.5]-



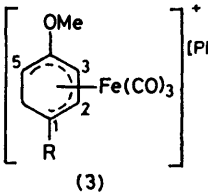
(1)

a; R = $CH(CO_2Me)_2$ or CN
b; R = $CH_2CO_2Et$
c; R = $CH_2CO_2Me$



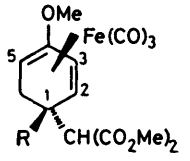
(2)

a; R = Me, $R^1$ = $CH(CO_2Me)_2$ or CN
b; R = $[CH_2]_2CO_2Me$, R' = $CH(CO_2Me)_2$
c; R = Me, $R^1$ = $CH_2CO_2Me$
d; R = $[CH_2]_2CO_2Me$, $R^1$ = $CH_2CO_2Me$
e; R = $[CH_2]_3CO_2Me$, $R^1$ = $CH(CO_2Me)_2$
f; R = $[CH_2]_3CO_2Me$, $R^1$ = $CH_2CO_2Me$



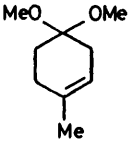
(3)

a; R = Me
b; R = $[CH_2]_2CO_2Me$
c; R = $[CH_2]_3CO_2Me$



(4)

a; R = Me
b; R = $[CH_2]_2CO_2Me$
c; R = $[CH_2]_3CO_2Me$



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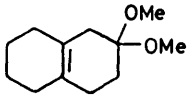

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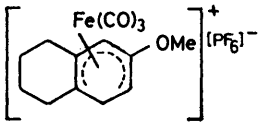

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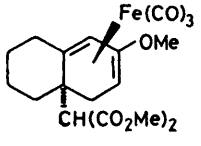


(8)

decane ring system has attracted much attention recently, a number of successful methods having been devised.[3] The spiro[5.5]undecane ring system also constitutes the basic structure of a number of terpenoids,[4] and there are several methods available for the synthesis of such compounds.[5] Since these are not always applicable to highly substituted derivatives, it is of interest to have alternative methods available.

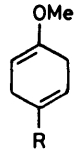
It was recently shown that 4,4-disubstituted cyclohexenones, or their related dienol ethers, such as (1a) or (2a) may be efficiently synthesised by reaction of nucleophiles such as $^-CH(CO_2R)_2$ and $CN^-$ with tricarbonylcyclohexadienyliumiron salts such as (3a).[6] These reactions lead to tricarbonyliron complexes of structure (4a), and removal of the $Fe(CO)_3$ moiety results in formation of (2a). The alternative approach to similar systems involves addition of the carbene obtained from diazoacetic ester to the double bond of the acetal (5), followed by deacetalisation and opening of the cyclopropane ring to give (1b). This method is unsuccessful when applied to the simple bicyclic derivative (6),[7] whereas I have previously shown[6] that exclusive addition of sodio-dimethylmalonate to the angular dienyl terminus of (7) occurs to give (8), so that a route involving tricarbonyldienyliumiron salts appears to offer considerable advantages in the construction of such molecules. Furthermore, since the reaction of these complexes with nucleophiles is stereospecific, occurring *exo* to the $Fe(CO)_3$ group,[8] prior resolution of these salts (which has not yet been achieved) would lead to an asymmetric synthesis of the desired compounds.

The above observations suggested a strategy which might be usefully applied to the synthesis of the aforementioned spirocyclic compounds *via* intermediates of structure (3b) and (3c). The present paper describes the results of initial studies in this direction, which represents the first approach to rational organic synthesis using tricarbonyldienyliumiron complexes.

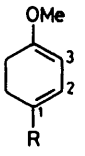
## RESULTS AND DISCUSSION

*Methyl 8-Methoxy-2-oxospiro[4.5]deca-6,8-diene-3-carboxylate* (14).—Lithium–ammonia reduction of *p*-methoxycinnamic acid led directly to the diene (9a, R = H) in 95% yield, which was fairly unstable and so was immediately treated with dimethyl sulphate to give the ester (9a, R' = Me). The $^1H$ n.m.r. spectra of the acid and of the crude ester indicated no other dienes to be present, but distillation of the ester resulted in the formation of a mixture of (9a, R' = Me) and the isomer

(10a). However, this is no disadvantage to the proposed complex formation, since conjugation of the 1,4-diene is

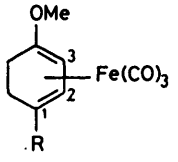


(9) a; R = $[CH_2]_2CO_2R^1$
b; R = $[CH_2]_3CO_2R^1$



(10) a; R = $[CH_2]_2CO_2Me$
b; R = $[CH_2]_3CO_2Me$

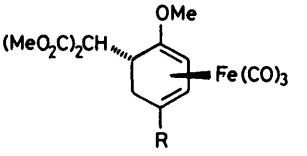
necessary during the course of this reaction. Consequently, the mixture of esters was treated with pentacarbonyliron under the usual conditions, giving after chromatography a yellow oil, the $^1H$ n.m.r. spectrum of which indicated the presence of >90% of the desired complex (11a), together with minor amounts of aromatic material. This behaviour contrasts with that found previously for complexation of simple substituted cyclohexadienes which invariably give almost equimolar mixtures of isomers.[9] A pure sample of (11a) could be



(11) a; R = $[CH_2]_2CO_2Me$
b; R = $[CH_2]_3CO_2Me$

obtained by crystallisation from hexane at low temperature, and showed the expected $^1H$ n.m.r. signals for the 4-methoxy-group (δ 3.45), and the typical AB pattern for 2-H and 3-H (details in the Experimental section). Reaction of (11a) with triphenylmethylium tetrafluoroborate in dichloromethane did not proceed so readily as for simpler complexes [6,9] and elevated reaction temperatures were necessary for appreciable yields. Attempted precipitation of the tetrafluoroborate salts from the reaction mixture by addition of excess of diethyl ether led to the formation of an oil, which was extracted into the minimum volume of water, and the salts re-precipitated by addition of a small excess of aqueous ammonium hexafluorophosphate. Recrystallisation of the resulting complex from dichloromethane–ether gave moderate yields (62%) of the pure hexafluorophosphate (3b), also obtainable by similar treatment of crude (11a). Apparently, contaminant compounds either do not react with the trityl cation, or else any resulting minor products remain in solution during precipitation. This is useful, since losses of (11a) during recrystallisation can thus be avoided. The salt (3b) was readily identified from its $^1H$ n.m.r. spectrum, which was directly comparable to the spectra of similar compounds.[6,9]

Treatment of (3b) with sodio-dimethylmalonate followed by column chromatography gave in 88% yield a yellow oil, which was a single spot on t.l.c., but which was shown by $^1H$ n.m.r. spectroscopy to consist of *ca.* 80% of the desired triester complex (4b) together with a second component which was presumed to be (12a) owing to the presence of the partly obscured AB quartet corresponding to 2-H and 3-H (see Experimental section). This compound is formed by addition of carbanion to (3b) at the unsubstituted terminus C-5, a pathway which was not observed for the simpler analogue (3a),[6] and which therefore shows the sensitivity of regioselectivity to the nature of the 1-substituent present in the cation. Repeated crystallisation from hexane at −50 °C produced only 95% pure (4b), and



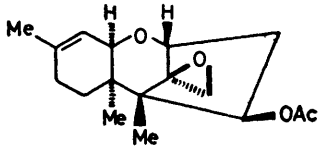
(12)a; R = $[CH_2]_2CO_2Me$
b; R = $[CH_2]_3CO_2Me$

since severe losses are incurred in such a process it was decided to carry both triesters through the next stages in anticipation that a readily separable mixture would be formed in the ultimate cyclisation step, as was indeed the case (see below). Again, complex (4b) had $^1H$ n.m.r. spectrum directly comparable to the previously characterised analogues.

The triester (2b) was readily liberated in 77% yield by treatment of (4b) with trimethylamine *N*-oxide in refluxing benzene,[10] the minor amount of aromatic material present in the product presumably arising from (12a). The major component (2b) showed the expected $^1H$ n.m.r. signals, 2-H and 3-H now being almost coincident [*cf.* complex (4b)] and occurring as a close multiplet at δ 5.80, whilst the vinyl ether proton 5-H is found as a broad multiplet at the characteristically high field of δ 4.55. The triester singlets occurred at δ 3.72, 3.69, and 3.66 and the remaining 4-methoxy at δ 3.53, again comparable with [2a, R′ = $CH(CO_2Et)_2$]. As expected, this compound could not be cyclised by base treatment, since equilibrium lies in favour of the carbanion derived from the *gem*-diester group. Consequently, it was necessary to effect its decarbomethoxylation to give a diester capable of undergoing Dieckman cyclisation. Furthermore, a reaction involving acidic work-up conditions was undesirable, since the enol ether group already present in the molecule represented an attractive ketone protection for the subsequent base treatment, without involving losses in hydrolysis and re-protection. With this in mind, the use of tetramethylammonium acetate in hot hexamethylphosphoramide (HMPA) for effecting the conversion was examined.[11]

At this stage it was appropriate to establish the required decarbomethoxylation reaction conditions using a suitable readily available model compound. For this purpose it was decided to use the diester [2a, R′ = $CH(CO_2Me)_2$] since this material was already available

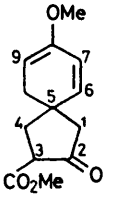
from previous studies, and also because acidic hydrolysis of the product (2c) would result in the enone monoester (1c) which is analogous to the already prepared ethyl ester (1b).[7] Furthermore, since (1b) has itself been used as an intermediate for the synthesis of trichodermin (13),[12] a member of the trichothecane group of sesquiterpenoid antibiotics, then this diversion would be exceed-




(13)

ingly useful in establishing application of complexes such as (3) in rational synthesis. It was found that the volume of solvent used in the reaction was fairly critical. Small-scale experiments using a relatively large excess of HMPA required much shorter times than did larger-scale experiments employing somewhat higher concentrations of the diester, and prolonged heating in the former cases led to much loss of material. For example, a 2.4% w/v solution of diester in HMPA at 100 °C produced, after 5.5 h, the desired monoester in 54% yield. A similar concentration of diester heated for 16 h gave only 10% yield of monoester. On the other hand, a 15% solution of diester treated with a 10% molar excess of tetramethylammonium acetate required 12 h at 100 °C for completion, whereupon a 70% yield of (2c) was obtained (these conditions are slightly different to those used by Trost and Verhoeven [11]). Treatment of this compound with dilute hydrochloric acid in tetrahydrofuran at 0 °C produced, after purification on preparative layer chromatography, a 55—60% yield of (1c) as a colourless oil, the spectroscopic properties of which agreed with the published data for the analogous ethyl ester (1b).[7,12]

Similar treatment of the crude triester (2b) with tetramethylammonium acetate gave a 77% yield of the diester (2d), still containing a minor amount of aromatic impurity. This compound gave two spots on t.l.c. and preparative layer chromatography allowed the isolation of pure (2d), which showed the anticipated spectral properties. Since this compound was somewhat susceptible to enol ether hydrolysis on silica gel, preparation of pure material in yields suitable for cyclisation studies was impractical. Consequently, crude (2d) was treated directly with sodium hydride in dry THF using fairly standard conditions.[13] Aqueous work-up afforded an alkaline solution which was extracted with ether to give a small amount of material, t.l.c. examination of which showed the presence of five compounds, none of which corresponded to the cyclisation product, or starting material. Neutralisation of the residual aqueous phase with 50% acetic acid, followed by ether extraction and rapid chromatography on Florisil, afforded a single product (t.l.c.) as a colourless oil, the rather low yield (30—40%) being acceptable in view of the fact that it was derived from crude precursor. This compound was assigned the structure (14) on the basis of the following considerations. Its ready solubility in aqueous alkali (work-up) suggested the presence of a five-membered-ring β-keto-ester. That the ketone function occurred in a five-membered ring was indicated by the presence of a band at 1 758 $cm^{-1}$ in the i.r. spectrum, with the ester CO at 1 730 $cm^{-1}$. This compares well with the spectrum of ethyl cyclopentanone-2-carboxylate, which shows a ring CO at 1 750 and an ester CO at 1 730 $cm^{-1}$,[14] and with the spectrum of similar spiro[4.5]decane β-keto-ester derivatives giving ring CO bands at 1 764 $cm^{-1}$ and ester CO at 1 715 $cm^{-1}$.[15] The mass spectrum showed the expected molecular ion at *m/e* 236. In the $^1H$ n.m.r. spectrum the diene proton resonances were almost identical to those of (2d) except that 2-H and 3-H formed a much narrower multiplet. Only one ester methoxy and one enol ether methoxy signal was observed, indicating the presence of only one diastereoisomer, presumably due to its formation by reversible protonation of the enolate anion. The structure (14),

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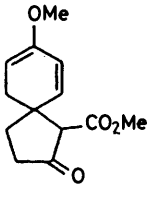
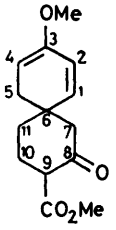



(15)

rather than (15), was indicated by the presence of a doublet of doublets (integrated intensity 0.8 H due to keto-enol tautomerism [15]) at δ 3.27, due to the β-keto-ester methine proton 3-H adjacent to a methylene group.

*Methyl 3-Methoxy-8-oxospiro*[5.5]*undeca-1,3-diene-9-carboxylate* (16).—A series of reactions identical to the above was employed, commencing with 4-(*p*-methoxyphenyl)butyric acid. Birch reduction of this compound, followed by esterification and distillation, gave a mixture of 1,4- and 1,3-dienes (9b, R′ = Me) and (10b), which were treated with pentacarbonyliron to give, after chromatography, the complex (11b), 90—95% pure. This compound defied all crystallisation attempts, not surprising in view of the fact that the corresponding carboxylic acid, readily available by treatment of (11b) with aqueous ethanolic potassium hydroxide, melted at a much lower temperature (86.5—88 °C) than that derived from (11a) (m.p. 120.5—122 °C).[16] Consequently, complex (11b) is expected to have a much lower m.p. than (11a) (m.p. 34.5—35.5 °C). Treatment of (11b) with triphenylmethylium tetrafluoroborate again required elevated temperatures, and gave the hexafluorophosphate (3c) after work-up similar to that used for (3b). Reaction of this with sodio-dimethylmalonate at 0 °C gave an inseparable mixture of triesters [(4c) 75—80%] and [(12b) 20—25%]. In this particular reaction, it was found that regioselectivity of carbanion addition was only marginally influenced by temperature, reaction at −78 °C giving a mixture now containing

85% of the desired isomer (4c). Treatment of the mixture of triester complexes with trimethylamine *N*-oxide gave the triester (2e) together with a minor amount of aromatic material derived from (12b), which could be separated by preparative layer chromatography on silica gel to give a colourless oil with spectral properties anticipated for (2e) (see Experimental section). For the ultimate Dieckman cyclisation it was necessary to use pure diester (2f) in this case, since the resulting six-membered-ring β-keto-ester was not sufficiently acidic to remain in the alkaline solution produced during work-up, and simple purification as for (14) could not be effected. The diester (2f) was found to be somewhat more susceptible than (2e) to enol ether hydrolysis by prolonged exposure to silica gel, so that p.l.c. purification prior to decarbomethoxylation was undertaken. Treatment of pure (2e) with tetramethylammonium acetate in HMPA as above gave almost pure diester (2f) which was cyclised in 60% yield to a spiro[5.5]undecane derivative. The $^1$H n.m.r. spectrum of this compound showed the presence of only one isomer, assigned the structure (16)

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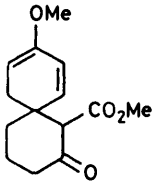


(17)

for the following reasons. The i.r. spectrum showed a band at 1 712 cm$^{-1}$ corresponding to the six-membered-ring ketone. The β-keto-ester methine proton 3-H gave a broad signal at δ 3.67 (unresolved coupling) in the n.m.r. spectrum, whilst the alternative structure (17) is expected to give a sharp singlet for this proton. This latter compound also has the ester group adjacent to the spiro-centre, which is consequently more sterically crowded, so that it is not the favoured isomer during a reversible cyclisation of the type used here.

The application of this type of reaction to form spiro-centres with more complex systems is currently being explored.

## EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 457, mass spectra with A.E.I. MS12 or MS30, and $^1$H n.m.r. spectra were recorded with Perkin-Elmer R12 (60 MHz) or Varian HA100 (100 MHz) instruments. All chromatographic operations with iron complexes were conducted under an atmosphere of nitrogen.

*Tricarbonyl*[η-1-(2′-*methoxycarbonylethyl*)-4-*methoxycyclohexa*-1,3-*diene*]*iron* (11a).—*p*-Methoxycinnamic acid [17] (50 g) was dissolved in a mixture of liquid ammonia (1 l) and t-butyl alcohol (150 ml) in a three-necked flask fitted with mechanical stirrer and a solid $CO_2$–acetone condenser. Lithium metal (17.5 g) was added in portions during 90 min, and the resultant blue mixture was stirred for a further 5 h. Sufficient ammonium chloride was added to discharge the colour, and the ammonia was allowed to evaporate overnight under a steady stream of nitrogen. The lithium salts were dissolved in ice–water and the cooled solution (0 °C) was slowly acidified to pH 4.5 by addition of formic acid with constant stirring. The product was extracted with ether in the usual way to give (9a, R = H) as a white solid (48 g, 94%); $\delta_H(CDCl_3)$ 10.72 (1 H, s, exchangeable, $CO_2H$), 5.37 (1 H, br s, vinyl-H), 4.57 (1 H, br s, vinyl-H), 3.47 (3 H, s, OMe), and 2.9—1.2 (8 H, methylene envelope). This compound was immediately treated with dimethyl sulphate (40 ml) in stirred refluxing acetone (500 ml) containing potassium carbonate (60 g) under nitrogen for 3.5 h. Filtration, removal of acetone, followed by the usual ether extraction procedure, and distillation, afforded the ester as a colourless liquid (34 g, 65%), b.p. 70—74 °C at 0.01 mmHg. The $^1$H n.m.r. spectrum showed this to be a mixture of (9a, R′ = Me, 19%) and (10a, 81%), $\delta_H(CDCl_3)$ 5.6 [d, *J* 6 Hz, vinyl-H of (10a)], 5.45 (br s, vinyl-H of (9a, R′ = Me)], 4.86 [d, *J* 6 Hz, vinyl-H of (10a)], 4.6 (br s, vinyl-H of (9a, R′ = Me)], 3.64 [s, $CO_2Me$ of both + OMe of (9a, R′ = Me)], 3.53 [s, OMe of (10a)], and 2.9—2.1 (8 H, methylene envelope). The ester (25 g) and pentacarbonyliron (100 ml) were refluxed in stirred dibutyl ether (250 ml) under nitrogen for a period of 7 h each day and allowed to stand at room temperature overnight. After 3 d (21 h reflux) the mixture was filtered through Celite and reaction continued in the same manner for a further 2 d (total reflux time 35 h). The mixture was again filtered through Celite, and dibutyl ether and unreacted pentacarbonyliron were removed on the rotary evaporator, unreacted ester (*ca.* 2—3 g) was removed at 100—115 °C (0.05 mmHg), and the residual complex was filtered through silica gel with benzene to give a yellow oil (20 g, 47%), the $^1$H n.m.r. spectrum of which showed it to be >90% pure (11a). A sample of this material was recrystallised from hexane at −10 °C to give pure (11a), m.p. 34.5—35.5 °C; $\nu_{max.}$(Nujol) 2 035, 1 955, and 1 738 cm$^{-1}$; $\delta_H(CDCl_3)$ 5.18 (1 H, d, $J_{2,3}$ 5 Hz, 2-H), 4.99 (1 H, d, $J_{2,3}$ 5 Hz, 3-H), 3.68 (3 H, s, $CO_2Me$), 3.45 (3 H, s, 4-OMe), and 2.60—1.50 (8 H, m, methylene envelope); *m/e* 336 ($M^+$) (Found: C, 50.10; H, 4.95. $C_{14}H_{16}FeO_6$ requires C, 50.03; H, 4.80%).

*Tricarbonyl*[η-1—5-1-(2′-*methoxycarbonylethyl*)-4-*methoxycyclohexa*-2,4-*dienylium*]*iron Hexafluorophosphate* (3b).—Triphenylmethylium tetrafluoroborate (600 mg) was added to a solution of the above pure complex (460 mg) in dry dichloromethane (10 ml) and the solution was refluxed under dry nitrogen for 1 h. The mixture was then poured into ether (50 ml) and the insoluble oil extracted with water (3 × 3 ml). To the combined aqueous extracts at 50 °C was added ammonium hexafluorophosphate (300 mg) in water (1 ml) and the mixture was cooled in ice. The yellow precipitate was filtered off, washed with a little water, and dried *in vacuo* to give the hexafluorophosphate (3b) (410 mg, 62%) which was pure as judged from the $^1$H n.m.r. spectrum. An analytical sample of (3b) was obtained by recrystallisation from dichloromethane–ether [identical treatment of crude (11a) gave material of the same quality but in correspondingly lower yield]; $\nu_{max.}$(Nujol) 2 118, 2 060, and 1 730 cm$^{-1}$; $\delta_H(CD_3CN)$ 6.79 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2.5 Hz, 3-H), 5.64 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), 3.91 (1 H, m, 5-H), 3.78 (3 H, s, $CO_2Me$), 3.64 (3 H, s, 4-OMe), 3.00 (1 H, dd, $J_{5,6}$ 6, $J_{gem}$ 15 Hz, *endo*-6-H), and 2.55—2.10 (5 H, m, *exo*-6-H and 2 $CH_2$) (Found: C, 34.95; H, 3.25. $C_{14}H_{15}F_6FeO_6P$ requires C, 35.03; H, 3.15%).

*Reaction of* (3b) *with Sodio-dimethylmalonate*.—This reaction was carried out in THF (dried with Na–benzophenone) under $N_2$ at 0 °C as previously described.[6] In a typical run the hexafluorophosphate (1.508 g) on work-up gave a yellow oil (1.350 g) which was chromatographed on silica gel with 5% ethyl acetate in benzene. A minor yellow band (20 mg) which eluted first was not identified, and the product was gradually eluted to give a yellow oil (1.28 g, 88%) which showed a single spot on t.l.c. in a number of solvent systems. From the $^1H$ n.m.r. spectrum this material was a mixture of two compounds, the major isomer (80%) being the desired triester (4b). Repeated crystallisation from dilute hexane solution at −50 °C gave *ca.* 95% pure (4b) in low yield, which remained liquid at normal temperatures; $\nu_{max.}$ (film) 2 040, 1 970, and 1 730 $cm^{-1}$; $\delta_H(CDCl_3)$ 4.97 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2 Hz, 3-H), 3.68 (6 H, s) and 3.65 (3 H, s) (3 $CO_2Me$), 3.57 (3 H, s, 4-OMe) (total integrated intensity of OMe region 13 H due to obscured malonate methine singlet), 3.35 (2 H, m, 2-H and 5-H), and 2.75—1.50 (6 H, m, methylene envelope); *m/e* 466 ($M^+$). The minor component of the mixture showed doublets ($J_{AB}$ 6 Hz) at δ 5.40 and 5.10, the latter signal being partly obscured, indicating that this compound is (12).

*Ethyl* (1-*Methyl*-4-*oxocyclohex*-2-*enyl*)*acetate* (1b).—The dimethyl ester [2a; R′ = $CH(CO_2Me)_2$] was obtained as previously described for the diethyl ester [6] (yield 65—68%) from the hexafluorophosphate (3a). This compound (2.822 g) was stirred with tetramethylammonium acetate [18] (1.965 g) in HMPA (20 ml) at 100 °C under nitrogen for 12 h. The mixture was cooled, poured into water (200 ml) and extracted with ether (3 ×). The extracts were washed with water, saturated sodium hydrogen carbonate solution, and again with water, and dried ($MgSO_4$). The solvent was removed at reduced pressure and the residue was washed through a short Florisil column with ether to yield the monoester (2c) (1.55 g, 71%); $\nu_{max.}(CHCl_3)$ 1 732, 1 660, and 1 612 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.72 (2 H, m, 2-H and 3-H), 4.55 (1 H, m, 5-H), 3.63 (3 H, s, $CO_2Me$), 3.52 (3 H, s, 4-OMe) 2.4—2.1 (4 H, methylene), and 1.13 (3 H, s, Me); *m/e* 196 ($M^+$). This compound (1.37 g) was dissolved in tetrahydrofuran (20 ml) at 0 °C, and 5% aqueous hydrochloric acid (4 ml) was added. The mixture was stirred for 40 min at 0 °C, poured into water (100 ml) and neutralised with aqueous sodium hydrogen carbonate. Ether extraction afforded the ketone (1b) (0.85 g) (*ca.* 92% pure by n.m.r.). Preparative layer chromatography on silica gel, using 20% ethyl acetate in benzene, gave pure (1b) (0.72 g, 57%), as a colourless oil; $\nu_{max.}(CHCl_3)$ 1 738 and 1 680 $cm^{-1}$; $\delta_H(CDCl_3)$ 6.80 (1 H, br d, 2-H), 5.85 (1 H, d, $J_{2,3}$ 10 Hz, 3-H), 3.65 (3 H, s, $CO_2Me$), 2.45 (2 H, s, acetate-$CH_2$), 2.5—1.8 (4 H, m, 2 $CH_2$), and 1.27 (3 H, s, Me); *m/e* 182 ($M^+$).

*Preparation of Diester* (2d).—The crude complex (4b) (4.60 g) was refluxed vigorously in benzene (100 ml) together with anhydrous trimethylamine *N*-oxide (7.0 g) for 8 h, after which time the i.r. spectrum of the mixture showed no bands due to $Fe(CO)_3$. The mixture was filtered and the benzene solution was washed with water (3 ×) and dried ($MgSO_4$). Removal of solvent at reduced pressure, followed by rapid filtration of a concentrated ether solution through a short Florisil column gave the crude triester (2b) (2.38 g, 74%) as a colourless oil; $\nu_{max.}$ (benzene) 1 738, 1 682, and 1 610 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.80 (2 H, m, 2-H and 3-H), 4.55 (1 H, br m, 5-H), 3.72, 3.69, and 3.66 (3 $CO_2Me$), 3.53 (3 H, s, 4-OMe), and 2.8—1.9 (6 H, methylenes) (malonyl methine obscured by $CO_2Me$ peaks); *m/e* 326 ($M^+$).

This compound (0.69 g) was stirred with tetramethylammonium acetate (0.31 g) in HMPA (8 ml) for 11.5 h at 100 °C under nitrogen. Work-up as above afforded the crude diester (2d) (0.372—0.411 g, 66—73%) as a colourless oil. An analytical sample of this compound was obtained by preparative layer chromatography on silica gel, using 15% ethyl acetate in benzene; $\nu_{max.}(CHCl_3)$ 1 735, 1 660, and 1 612 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.73 (2 H, m, 2-H and 3-H), 4.55 (1 H, m, 5-H), 3.65 and 3.63 (each 3 H, s, 2 $CO_2Me$), 3.52 (3 H, s, 4-OMe), 2.50—1.65 (8 H, methylene envelope); *m/e* 268 ($M^+$) (Found: C, 62.25; H, 7.20. $C_{14}H_{20}O_5$ requires C, 62.67; H, 7.51%).

*Dieckman Cyclisation of Diester* (2d).—Sodium hydride (200 mg, 50% dispersion in mineral oil) was washed with dry pentane (5 × 2 ml) under nitrogen. THF (dried by Na–benzophenone) (5 ml) was added *via* a rubber septum and the mixture was stirred at room temperature whilst a solution of crude (2d) (284 mg) in dry THF (5 ml) was added. Stirring was continued at room temperature overnight and then at reflux temperature for 2 h. A solution of methanol in ether was added to consume any excess of sodium hydride, and the mixture was poured into water (25 ml). The alkaline solution was extracted with ether (3 ×) and the ether layer was discarded after t.l.c. examination. The stirred aqueous phase was neutralised (pH 6) by dropwise addition of 50% aqueous acetic acid, and the product extracted in the usual way with ether. The yellow oil so obtained was chromographed with ether on a small column of Florisil to give the spiro[4.5]decane derivative (14) as a colourless oil (80—100 mg, 30—40%), which was a single spot on t.l.c.; $\nu_{max.}(CHCl_3)$ 1 758, 1 730, 1 658, and 1 610 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.75 (2 H, m, 6-H and 7-H), 4.55 (1 H, m, 9-H), 3.73 (3 H, s, $CO_2Me$), 3.52 (3 H, s, 8-OMe), 3.27 (0.8 H, keto-enol tautomerism, dd, $J_{3,4}$ 8, $J_{3,4'}$ 3 Hz, 3-H), and 2.5—2.1 (6 H, methylene envelope); *m/e* 236.105 3 ($M^+$) ($C_{13}H_{16}O_4$ requires *M*, 236.104 8).

*Tricarbonyl*[η-1-(3′-*methoxycarbonylpropyl*)-4-*methoxycyclohexa*-1,3-*diene*]*iron* (11b).—4-(*p*-Methoxyphenyl)-butyric acid, prepared by standard literature methods [19] (19.0 g), was treated with lithium metal (4.0 g) in liquid ammonia (400 ml) containing t-butyl alcohol (30 ml) in the manner described above to give the white crystalline acid (9b, R′ = H) (18.5 g, 96%); $\nu_{max.}$(Nujol) 3 500—2 300, 1 705, 1 663, and 1 610 $cm^{-1}$; $\delta_H(CDCl_3)$ 9.3 (1 H, s, $CO_2H$), 5.35 (1 H, br s, vinyl), 4.57 (1 H, br s, vinyl), 3.46 (3 H, s, OMe), and 2.8—1.5 (10 H, methylene). The crude acid (18.0 g) was treated with dimethyl sulphate (10 ml) and potassium carbonate (30 g) in stirred refluxing acetone (200 ml) under nitrogen. Ether extraction furnished the crude ester (9b, R′ = Me) (18.0 g, 93%); $\delta_H(CDCl_3)$ 5.33 (1 H, br s, vinyl), 4.55 (1 H, br s, vinyl), 3.57 (3 H, s, $CO_2Me$), 3.45 (3 H, s, OMe), and 2.7—1.5 (10 H, methylene).

Distillation of this compound gave a mixture of (9b, R′ = Me) (15%) and (10b) (85%) (14.0 g, 72%), b.p. 90—102 °C at 0.05 mmHg; $\nu_{max.}$(film) 1 735, 1 658, and 1 610, $cm^{-1}$; $\delta_H(CDCl_3)$ (10b) 5.55 (1 H, d, *J* 6 Hz, 2-H), 4.83 (1 H, d, *J* 6 Hz, 3-H), 3.60 (3 H, s, $CO_2Me$), 3.50 (3 H, s, OMe), and 2.8—1.5 (10 H, methylene). This mixture (13.0 g) was treated with pentacarbonyliron (40 ml) in dibutyl ether in the manner described above for (11a), using a total reflux time of 44 h, and gave after work-up [6] unreacted dienes (3.0 g, 23%). Chromatography on silica gel gave a yellow oil (9.0 g, 41%), the n.m.r. spectrum of which showed it to

contain at least 90 mol % of (11b). This could not be crystallised and preparative layer chromatography gave only slight improvement of purity (95%); $\nu_{max.}$(film) 2 030, 1 945, and 1 730 $cm^{-1}$; $\delta_H$ 5.15 (1 H, d, *J* 5 Hz, 2-H), 4.90 (1 H, d, *J* 5 Hz, 3-H), 3.62 (3 H, s, $CO_2Me$), 3.38 (3 H, s, OMe), and 2.5—1.4 (10 H, methylenes); *m/e* 350 ($M^+$).

*Tricarbonyl*[η-1—5-1-(3′-*methoxycarbonylpropyl*)-4-*methoxycyclohexa*-2,4-*dienylium*]*iron Hexafluorophosphate* (3c).—The crude complex (11b) (5.0 g) was treated with triphenylmethylium tetrafluoroborate (6.0 g) in refluxing dichloromethane (120 ml) under nitrogen for 1.5 h. Work-up as for (3b) gave the hexafluorophosphate (3c) as yellow needles from dichloromethane–ether (3.7 g, 52%); $\nu_{max.}$ (Nujol) 2 115, 2 055, and 1 730 $cm^{-1}$; $\delta_H(CD_3CN)$ 6.82 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2.5 Hz, 3-H), 5.61 (1 H, br d, $J_{2,3}$ 6 Hz), 3.94 (1 H, ddd, $J_{5,5\text{-}endo}$ 6.5, $J_{5,6\text{-}exo}$ 1.5, and $J_{3,5}$ 2.5 Hz, 5-H), 3.80 (3 H, s, $CO_2Me$), 3.64 (3 H, s, OMe), 3.00 (1 H, ddd, $J_{gem}$ 15, $J_{5,6\text{-}endo}$ 6.5, $J_{2,6\text{-}endo}$ 1.0 Hz, *endo*-6-H), and 2.5—1.4 (7 H, *exo*-6-H and 3 $CH_2$) (Found: C, 36.60; H, 3.55. $C_{15}H_{17}F_6FeO_6P$ requires C, 36.46; H, 3.4%).

*Triester Complex* (4c).—The hexafluorophosphate (3c) (2.93 g) was treated in the usual way [6] with sodio-dimethylmalonate in THF, but using a reaction temperature of −78 °C. Aqueous work-up and ether extraction followed by column chromatography on silica gel gave a single yellow band which was eluted with 10% ethyl acetate in benzene, to produce a yellow oil (2.60 g, 91%) which contained (4c) (85%) and (12b) (15%) and which gave a single spot on t.l.c.; $\nu_{max.}(CHCl_3)$ 2 055, 1 970, 1 755 (sh), and 1 733 $cm^{-1}$; $\delta_H(CDCl_3)$ (4c) 4.97 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 3 Hz, 3-H), 3.72, 3.70, 3.67 (10 H, 3 $CO_2Me$ and malonyl methine obscured), 3.61 (3 H, s, 4-OMe), 3.3 (2 H, m, 2-H and 5-H), and 2.9—1.4 (8 H, methylene) [doublets (*J* 5 Hz) at δ 5.25 and 4.85 (obscured) correspond to 2-H and 3-H of (12b)]; *m/e* 480 ($M^+$).

*Triester* (2e).—The complex (4c) (910 mg) was refluxed for 7 h in benzene (50 ml) with trimethylamine *N*-oxide monohydrate (2.0 g) using a water separator. Work-up as for (2b) gave the crude triester (2e) (560 mg, 87%) containing aromatic impurities derived from (12b). Preparative layer chromatography on neutral silica gel with 10% ethyl acetate in benzene furnished (2e) (385 mg, 60%); $\nu_{max.}$(film) 1 740, 1 657, and 1 610 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.85 (2 H, AB quartet, 2-H and 3-H), 4.55 (1 H, m, 5-H), 3.75, 3.71, and 3.68 (10 H, 3 $CO_2Me$ + obscured malonate methine), 3.55 (3 H, s, 4-OMe), and 2.6—1.5 (8 H, methylenes); *m/e* 340 ($M^+$) (Found: C, 59.80; H, 7.35. $C_{17}H_{24}O_7$ requires C, 59.99; H, 7.11%).

*Preparation and Dieckman Cyclisation of Diester* (2f).—The triester (2e) (300 mg) was stirred with tetramethylammonium acetate (140 mg) in HMPA (3 ml) at 100 °C under nitrogen for 12 h. Work-up as for (2d), followed by rapid elution through Florisil with ether, afforded the diester (2f) as a colourless oil (170 mg, 68%); $\nu_{max.}$(film) 1 740, 1 657, 1 610 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.70 (2 H, close AB multiplet, 2-H, 3-H), 4.50 (1 H, m, 5-H), 3.63 (6 H, s, 2 $CO_2Me$), 3.50 (3 H, s, 4-OMe), and 2.3 and 1.55 (10 H, m, methylene); *m/e* 282 ($M^+$). This compound (165 mg) was stirred at room temperature overnight with pentane-washed sodium hydride dispersion (100 mg) in THF (10 ml) under nitrogen, then at reflux temperature for 4 h. After destruction of excess of sodium hydride with an ether solution of methanol, the reaction mixture was poured into water and the product extracted with ether. Elution of the concentrated ether solution through Florisil afforded the spiro[5.5]undecane derivative (16) as a colourless viscous oil, *ca.* 95% pure (n.m.r., t.l.c.) (87 mg, 60%). An analytical sample was prepared by micro-distillation using an oven temperature of 110—120 °C at a pressure of 0.005 mmHg; $\nu_{max.}(CHCl_3)$ 1 735, 1 712, 1 658, and 1 615 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.50 (2 H, close AB multiplet, 7-H, 8-H), 4.55 (1 H, m, 10-H), 3.74 (3 H, s, $CO_2Me$), 3.67 (1 H, m, 3-H), 3.53 (3 H, s, OMe), and 2.4—1.3 (8 H, methylene); *m/e* 250 ($M^+$) (Found: C, 67.45; H, 7.45. $C_{14}H_{18}O_4$ requires C, 67.18; H, 7.25%).

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