Organoiron Complexes in Organic Synthesis. Part 13.[1] Synthesis of 6,6-Disubstituted Tricarbonyl(cyclohexadienylium)iron Salts, and their Conversion into 4,4-Disubstituted Cyclohexa-2,5-dienones

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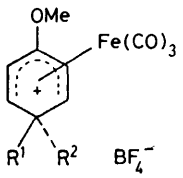
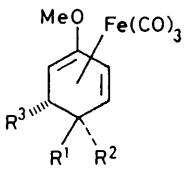
Oxidative cyclisation of cyclohexadiene–$Fe(CO)_3$ complexes having a hydroxy-group in the β-position of a 5-exo_{Fe}-substituent can be effected with either thallium(III) trifluoroacetate or iron(III) chloride on silica gel. The products were readily converted into the title compounds.

OUR recent discovery [2] that tricarbonylcyclohexadieneiron complexes bearing a β-hydroxylated substituent at C-5 can be oxidatively cyclised to give tetrahydrofuranoid derivatives prompted us to examine the potential application of this procedure to the preparation of hitherto unobtainable cyclohexadienylium complexes such as (1) having a quaternary C-6 centre. Such compounds can not be prepared by hydride abstraction from *gem*-disubstituted complexes such as (2) owing to steric factors.[3] We were initially interested in this type of





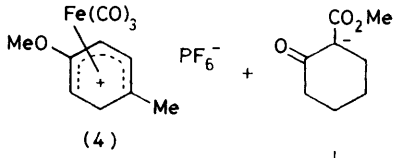
(2) $R^1, R^2 \neq H, R^3 = H$

(3) $R^1, R^2\ R^3 \neq H$

dienylium complex in order to study the limitations on nucleophile addition, which normally proceeds stereospecifically at the exo_{Fe} face (opposite the metal atom).[4,†] Thus with very bulky substituents R^2 the question arises as to whether a nucleophile would now add $endo_{Fe}$. Furthermore, successful addition of a carbon nucleophile would be expected to provide an entry into complexes such as (3), which might serve as valuable intermediates in a number of synthetic projects in which we are currently involved.

RESULTS AND DISCUSSION

Oxidative Cyclisations.—Our starting point was the diastereoisomeric keto-ester complexes (5) and (6),[5] which we have previously prepared in quantitative yield from the dienylium complex (4) as shown. Each diastereoisomer was studied separately, although the subsequent experiments can be performed on the mixture. Sodium borohydride reduction occurred with *ca.* 85—90% stereoselectivity along the axial vector to give the major epimers (7) and (8), respectively, which were obtained pure by crystallisation. Examination of the liquors in each case indicated the presence of the axial alcohols (9) and (10), but at this juncture we did not isolate and fully characterise these minor components. The stereochemistries were readily ascertained by inspection of the i.r. spectra of (7) and (8) and of their derived methoxymethyl ethers (11) and (12). Thus, the ester peaks for the unprotected hydroxy-derivatives



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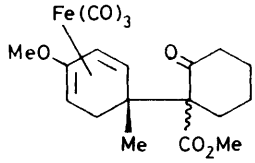
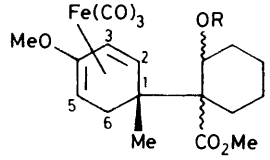


(5) α-CO_2Me

(6) β-CO_2Me



(7) α-CO_2Me, OR = α-OH

(8) β-CO_2Me, OR = β-OH

(9) α-CO_2Me, OR = β-OH

(10) β-CO_2Me, OR = α-OH

(11) α-CO_2Me, OR = α-OCH_2OMe

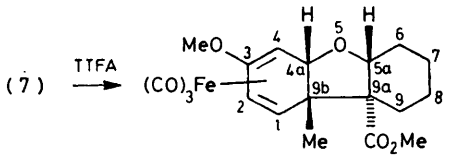
(12) β-CO_2Me, OR = β-OCH_2OMe

occur at *ca.* 1 700 cm^{-1}, whilst the methoxymethyl ether derivatives show the ester absorption at *ca.* 1 730 cm^{-1}. The recrystallisation liquors from (7) gave i.r. absorptions at 1 700 cm^{-1} [due to (7)] and at 1 720 cm^{-1}, the latter indicating the presence of the axial OH epimer (9), whilst the n.m.r. spectrum indicated the presence of two iso-

† The prefixes *exo* and *endo* have been used to denote stereochemistry in metal complexes for some time, but they are not entirely satisfactory when compared with their application to organic structures. The terms exo_{Fe} and $endo_{Fe}$ give a clearer indication of stereochemical relationships between metal and substituents on the ligand. See also B. F. G. Johnson, J. Lewis, D. G. Parker, and G. R. Stephenson, *J. Organomet. Chem.* 1980, **197**, 77.

meric compounds as a 1 : 1 mixture. Thus, hydrogen-bonding between the ester group and the *cis*-OH reduces the carbonyl stretching frequency of (7), and removal of the hydrogen-bonding by ether formation results in raising of this frequency, as expected.

To effect oxidative cyclisation of the OH group of (7)



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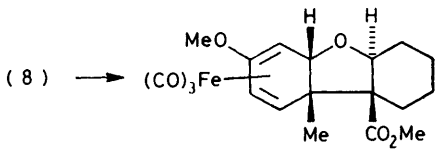
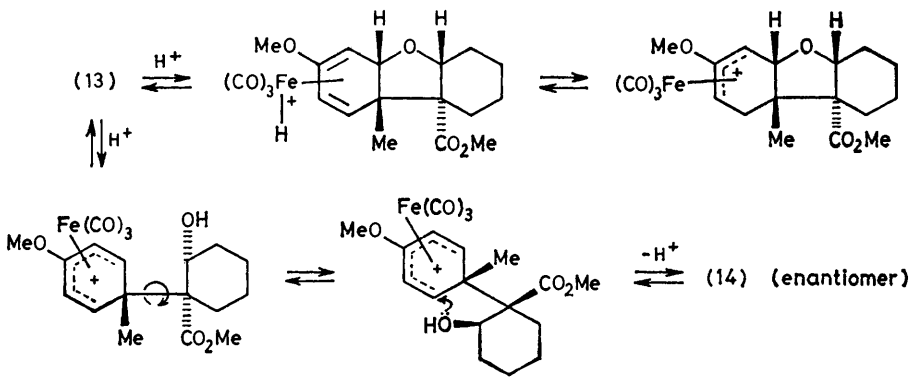


(14)

or (8) onto the diene–$Fe(CO)_3$ unit there were two methods at our disposal: treatment with thallium(III) trifluoroacetate [2a] (TTFA) or with iron(III) chloride on silica gel.[2b] The latter reagent has also been found useful recently for oxidative coupling of aromatic compounds.[6] When isomer (7) was treated with buffered TTFA the oxidative cyclisation product was obtained, but in only 30—40% yield. The n.m.r. spectrum of this compound, when run immediately, showed a single diastereoisomer which was presumed to be (13) based on the probable concertedness of the cyclisation under these conditions. However, on standing in chloroform, which contains traces of acid, the single compound rapidly rearranged to an equimolar mixture of diastereoisomers (13) and (14). Treatment of hydroxy-ester (8) with TTFA gave initially the single diastereoisomer (14), but in only 32% yield, and which again rearranged to the same mixture of (13) and (14). Reaction of (7) with iron(III) chloride on silica gel gave directly the same mixture of diastereoisomers, in *ca.* 90% yield. The rearrangement of these compounds in the presence of acid may proceed by only one mechanism as shown in the Scheme. Clearly, the first mechanism shown in this Scheme, an accepted process for such complexes, can not proceed to give (14) from (13). This interconversion is only possible *via* opening of the oxygen ring, rotation about the C–C bond, and re-closure of the ring.

Sodium borohydride reduction of the keto-ester complex (15) [7] occurred stereospecifically at the less substituted face of the cyclopentanone ring to give, as expected, the hydroxy-ester (16), illustrating the well-known differences between five- and six-membered carbocyclic systems. This compound underwent smooth cyclisation on treatment with $FeCl_3$–silica gel to give a *single diastereoisomer* which did not undergo rearrangement on exposure to chloroform, reflecting the thermodynamic stability of this isomer compared with (13), which was assigned the structure (17) on the basis of its spectral data (Experimental section).

Inspection of Dreiding models indicates that this difference is most likely a consequence of unfavourable interaction between the protons on the cyclopentane ring α-face and the diene–$Fe(CO)_3$ moiety in the *unobserved* isomer (18) compared with the analogous (14) and with the observed product (17). Such non-bonded interactions do not occur in (14) due to the ability of the cyclohexane ring to adopt a full chair conformation, and to the different stereochemistry of the oxygen substituent. There are no such unfavourable interactions in (17) making this isomer considerably more stable than (18), whereas the difference in stability between (13) and (14) can be seen to be almost negligible. In constructing suitable models we have utilised our own *X*-ray crystallographic data [5,7,8] which show the cyclohexadiene–

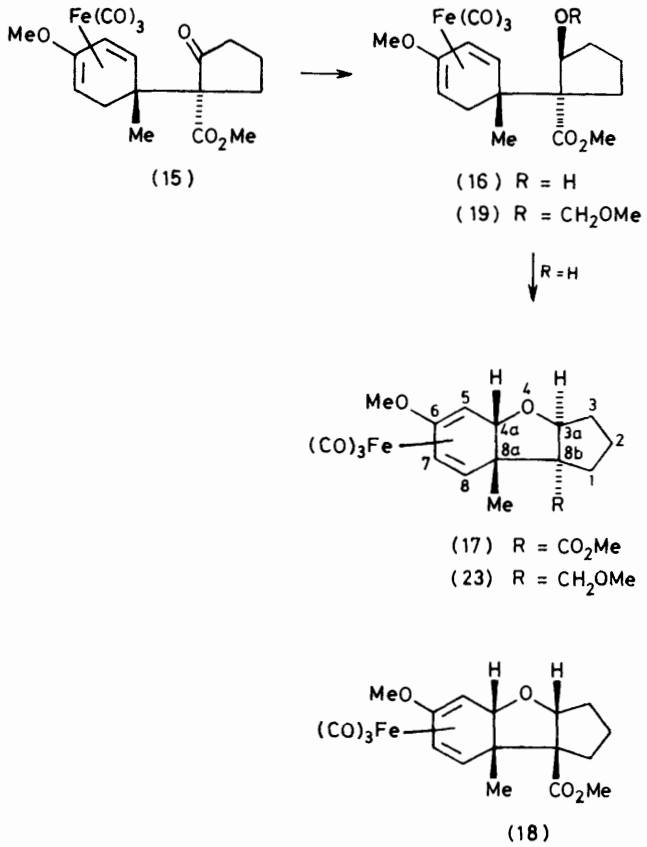


SCHEME

$Fe(CO)_3$ unit to have a shape very similar to the boat form of cyclohexene.

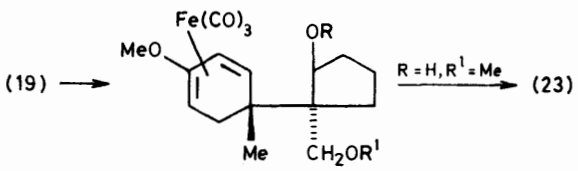
We also examined the cyclisation of the mono-protected diol (22), mainly for clarification of n.m.r. spectra of the later products (see below) and also as an illustration of selective protection. This compound was prepared from (16) by formation of the methoxymethyl ether (19), which was reduced to the primary alcohol (20) by di-

isobutylaluminium hydride, converted into the methyl ether (21) and thence to the secondary alcohol derivative (22). This was then cyclised to the complex (23) with



(15) (16) R = H (19) R = CH_2OMe (17) R = CO_2Me (23) R = CH_2OMe (18)

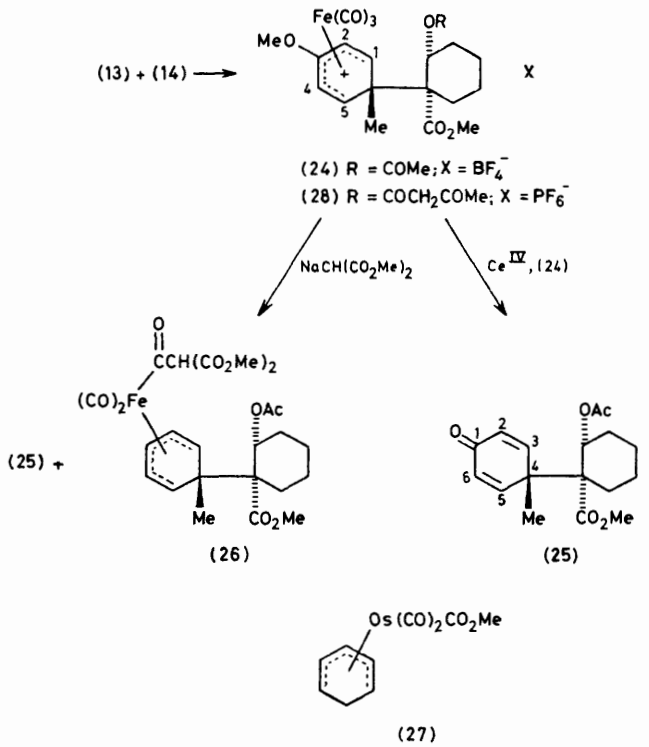
$FeCl_3$–silica gel. The use of methoxymethyl ether as alcohol protection on diene–$Fe(CO)_3$ complexes deserves comment. Firstly, it was found necessary to control the temperature of the reaction during the deprotection step (21) ⟶ (22): at too high a temperature acid-catalysed isomerisation of the diene–$Fe(CO)_3$ group occurs.[9] Secondly, we have used the tricarbonyliron



(20) R = CH_2OMe, R^1 = H
(21) R = CH_2OMe, R^1 = Me
(22) R = H, R^1 = Me

group as dienol ether protection, since it would not normally be possible to remove the methoxymethyl ether group in the presence of the more acid-labile enol ether. This is worth bearing in mind when planning a synthetic strategy employing these complexes.

Synthesis and Reactions of Dienylium Salts.—Treatment of the crude mixture of diastereoisomeric cyclised complexes (13) and (14), from the $FeCl_3$–silica reaction, with tetrafluoroboric acid–acetic anhydride resulted in ring-opening and acetylation of the hydroxy-function to give the 6,6-disubstituted cyclohexadienylium complex (24) in 66% overall yield from the hydroxy-ester derivative (7). The n.m.r. spectrum showed a single compound, as evidenced by the single peaks observed for each of the OMe, CO_2Me, OAc, and Me groups, but clearly showed the non-equivalence of 1-H and 5-H, and of 2-H and 4-H, expected as a result of the proximity of the asymmetric cyclohexane substituent. Small W-couplings were observed between these pairs of protons. We were unable to obtain any products of nucleophilic addition to the

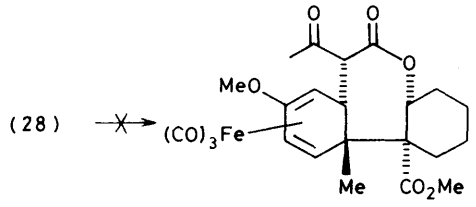


(24) R = COMe; X = BF_4^-
(28) R = $COCH_2COMe$; X = PF_6^-
(25) + (26) (25)

(27)

dienylium ligand from the reaction of (24) with dimethyl sodiomalonate or thiophenol in the presence of triethylamine; the latter we have previously found to add successfully to less highly substituted salts.[2a] A number of products were obtained, the major one being the dienone derivative (25) (see later) which possibly arises as a result of nucleophilic attack at the metal, followed by fragmentation of the resulting complex. This was the only product isolated (65% yield) from the thiophenoxide reaction at room temperature, probably reflecting the high affinity of sulphur nucleophiles for the metal. Whilst the dienone (25) was the major product of reaction of dimethyl sodiomalonate, we were able to isolate a minor product which had spectral properties consistent with the structure (26), the product of nucleophilic addition at a carbonyl ligand. The instability of this compound precluded rigorous purification for com-

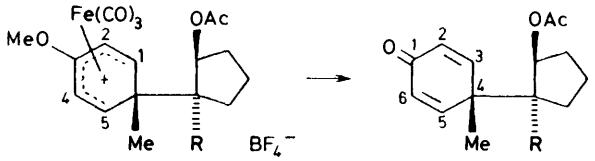
bustion analysis, but the n.m.r. spectrum was quite free from any major contamination. Unambiguous mass spectral data were not forthcoming, again due to thermal instability. However, the n.m.r. spectrum showed a pattern assignable to (26), all the dienylium protons being shifted to high field in comparison with the cationic analogues such as (24). Thus, 2-H and 4-H appeared coincidentally as a doublet (J 7 Hz) at δ 4.95, whilst 1-H and 5-H appeared as doublets of doublets with a 7 Hz vicinal coupling and a small W-coupling (2.5 Hz) to each other, comparable with (24), but at much higher field, δ 2.57 and 2.30 [*cf.* δ 4.04 and 3.60 in (24)]. The malonyl methine proton occurred as a sharp singlet at the distinctively low field of δ 5.23, reflecting considerable deshielding by the three flanking C=O groups. Had this group been attached directly to the metal we might have expected this proton to be slightly shielded relative to a normal malonyl methine group, in line with other iron(0) σ-complexes.[10] The methoxy-group resonated at δ 3.92, and the methyl group at δ 1.60, both slightly higher field than in (24). The remainder of the spectrum was as expected (Experimental section). Furthermore, the dienyl proton shieldings are similar to those reported for the osmium complex (27) [11a] which is, as far as we are aware, the only other example of this type of complex which has been subjected to n.m.r. analysis. This latter compound is unstable above 0 °C. The i.r. spectrum of (26) showed the metal carbonyl frequencies at 2 030 and 1 982 cm^{-1}, consistent with there being no nett positive charge on the metal, whilst there was observed an absorption of medium intensity at 1 690 cm^{-1}, close to the ester peaks at 1 738 and 1 725 cm^{-1}, and attributable to M–C=O stretching [*cf.* a band at 1 635 cm^{-1} observed for complex (27) [11a]]. An absorption at 1 533 cm^{-1}, similar to that given by (24), (28), (30), and (31), was consistent with the presence of the 3-methoxycyclohexadienyl ligand. Whilst this result is intrinsically interesting in



(29)

view of recent speculations concerning attack by nucleophiles at either the carbonyl ligand [11] or the metal [12] as a general mechanism of such reactions, it is not a synthetically useful process, and so we have pursued its study no further. An attempt to deliver the nucleophile intramolecularly, in a similar fashion to our previously reported spirocyclisation reactions,[13] required conversion of (13) and (14) into the acetoacetate-containing dienylium complex (28). This was readily achieved with keten dimer in the presence of tetrafluoroboric acid, but the resulting stable salt did not undergo cyclisation to the desired compound (29) on treatment with a number of bases, and instead gave (13) and (14), presumably *via* fragmentation of the keto-ester group, and a cyclohexadienone whose characterisation was not rigorously pursued. These products were evidence by chromatographic and i.r. properties.

Treatment of the cyclisation products (17) and (23) with tetrafluoroboric acid in acetic anhydride as above gave the tetrafluoroborates (30) and (31), respectively. Reaction of (31) with sodiomalononitrile, which we have previously shown to be less sterically demanding then dimethyl sodiomalonate in its reaction with dienylium complexes,[14] resulted in the formation of the



(30) R = CO_2Me
(31) R = CH_2OMe

(32) R = CO_2Me
(33) R = CH_2OMe

dienone derivative (33) as the only isolable product. Further reactions were not pursued. It is evident that *under no circumstances will irreversible nucleophilic addition occur at the* $endo_{Fe}$ *face*, in contrast with earlier observations on addition of methoxide where some *endo* product has been obtained.[11] The formation of cyclohexadienones in this way led us to investigate their direct formation by oxidative removal of the $Fe(CO)_3$ group. Whilst this has been effected with a number of mild oxidising agents for diene–$Fe(CO)_3$ complexes, no reports of similar reactions of dienylium complexes have appeared. Reaction of the tetrafluoroborates (24), (30), and (31) with cerium(IV) ammonium nitrate proceeded smoothly to give the dienones (25), (32), and (33), respectively, which were readily identified.

Thus, whilst the above dienylium salts are too hindered at the exo_{Fe} face to allow nucleophilic addition reactions, they are readily convertible to highly substituted cyclohexadienones. This complements existing methodology, such as *para*-alkylation of *para*-substituted phenolate anions, which is limited to fairly simple electrophiles,[15] and dehydrogenation of 4,4-disubstituted cyclohexenones (which are also readily accessible using our methodology) using, for example, phenylselenation–deselenation.[16]

EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 577, mass spectra with A.E.I. MS30, and ^1H n.m.r. spectra with Varian EM390 instruments. M.p.s were measured on a Kofler block and are uncorrected. All chromatographic operations were conducted under nitrogen.

Tricarbonyl[methyl 2-hydroxy-1-(2—5-η-4-methoxy-1-methylcyclohexa-2,4-dienyl)cyclohexanecarboxylate]iron, Diastereoisomers (7) *and* (8).—The procedure is described for the synthesis of (7), that for (8) being identical. The keto-ester complex (5) [5] (6.5 g) was stirred in dimethoxyethane–methanol (70 : 20; 90 ml) under nitrogen at 0 °C with sodium borohydride (1.7 g) for 7 h, when t.l.c. examination indi-

cated complete reaction. Aqueous work-up followed by ether extraction afforded the crude hydroxy-ester complex free from any ketonic starting material (6.6 g, 100%). Recrystallisation from 5% EtOAc–hexane afforded the pure single *epimer* (7), m.p. 107.5–109 °C (5.0 g, 77%). Chromatography of the liquors (SiO_2, 20% benzene–hexane) afforded an oil, homogeneous on t.l.c., the i.r. and n.m.r. spectra of which indicated a 1 : 1 mixture of the epimeric hydroxy-esters (7) and (9) (1.1 g, 17%, total yield 94%). Similarly, the keto-ester (6) (5.8 g) gave the pure *hydroxy-ester* (8), m.p. 83—84 °C (hexane), (4.1 g, 71%) and the epimeric mixture (8) and (10) (1.3 g, 22%). Spectral data: (7): $\nu_{max.}$ ($CHCl_3$) 3 530, 2 050, 1 975, 1 700, and 1 488 cm^{-1}; δ ($CDCl_3$) 4.95 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 2 Hz, 3-H), 3.75 (3 H, s, CO_2Me), 3.7 (1 H, m, C*H*OH), 3.6 (3 H, s, OMe), 3.2 (1 H, m, 5-H), 3.15 (1 H, d, $J_{2,3}$ 7 Hz, 2-H), 2.55 (1 H, dd, J_{gem} 15, $J_{5,6}$ 3 Hz, *endo*-6-H), 1.4 (1 H, dd, J_{gem} 15, $J_{5,6}$ 3 Hz, *exo*-6-H), 1.2 (3 H, s, Me), and 2.3—0.8 (9 H, m, OH and 4 × CH_2); *m/e* (%) 392 (30, $M^+ - CO$), 364 (10), 336 (65), and 318 (100) (Found: C, 54.7; H, 5.85. $C_{19}H_{24}FeO_7$ requires C, 54.33; H, 5.76%). Compound (8): $\nu_{max.}$ ($CHCl_3$) 3 540, 2 045, 1 970, 1 700, and 1 487 cm^{-1}; δ ($CDCl_3$) 5.10 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2 Hz, 3-H), 3.68 (3 H, s, CO_2Me), 3.58 (3 H, s, OMe), 3.23 (1 H, m, 5-H), 3.15 (1 H, d, J 12 Hz, C*H*OH), 2.6 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), 2.55 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, *endo*-6-H), 1.28 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, *exo*-6-H), 1.13 (3 H, s, Me), and 2.4—1.0 (9 H, OH and 4 × CH_2); *m/e* (%) 392 (25, $M^+ - CO$), 364 (10), 336 (60), and 318 (100) (Found: C, 54.4; H, 5.65. $C_{19}H_{24}FeO_7$ requires C, 54.33; H, 5.76%).

Tricarbonyl[*methyl* 1-(2—5-η-4-*methoxy*-1-*methylcyclohexa*-2,4-*dienyl*)-2-(*methoxymethoxy*)*cyclohexanecarboxylate*] *iron* (11).—This compound and the diastereoisomer (10) were used to verify the stereochemistry of the above products by comparison of i.r. spectra. The preparation and properties of (11) are described here, those for (10) being similar. The hydroxy-ester (8) (0.50 g) was refluxed under nitrogen in dry dichloromethane (10 ml) with di-isopropylethylamine (0.64 ml) and chloromethyl methyl ether (0.60 ml) for 7 h. The solution was cooled, water (5 ml) was added, and the mixture was stirred vigorously for 15 min, after which time the pale yellow organic layer was separated, washed twice with water, dried ($MgSO_4$), and evaporated to give the methoxymethyl ether as a yellow oil (0.53 g, 96%); $\nu_{max.}$ ($CHCl_3$) 2 045, 1 970, 1 730, and 1 488 cm^{-1}; δ ($CDCl_3$) 5.13 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2.5 Hz, 3-H), 4.78 and 4.63 (2 H, AB q, J 7 Hz, OCH_2O), 3.71 (3 H, s, CO_2Me), 3.64 (3 H, s, 4-OMe), 3.5 (1 H, m, C*H*OCH_2OMe), 3.42 (3 H, s, OMe), 3.28 (1 H, m, 5-H), 2.96 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, *endo*-6-H), 2.61 (1 H, d, J 6 Hz, 2-H), 1.40 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, *exo*-6-H), 1.16 (3 H, s, Me), and 2.4—1.0 (8 H). Since this compound was a viscous oil which could not be distilled, and could not be freed from traces of residual solvent, combustion analysis was not undertaken.

Tricarbonyl[*methyl* 2-*hydroxy*-1-(2—5-η-4-*methoxy*-1-*methylcyclohexa*-2,4-*dienyl*)*cyclopentanecarboxylate*]*iron* (16).—The keto-ester complex (15) [7] (2.0 g) was dissolved in methanol (60 ml) under nitrogen and cooled to 0 °C with stirring. With a back flush of nitrogen, sodium borohydride (0.5 g) was added and the mixture was stirred for 1 h at 0 °C. Aqueous work-up and ether extraction afforded the *hydroxy-ester* (16) as a single epimer, m.p. 118—119 °C (hexane) (1.94 g, 97%); $\nu_{max.}$ ($CDCl_3$) 3 620, 3 600—3 300, 2 052, 1 977, 1 719, and 1 489 cm^{-1}; δ ($CDCl_3$) 5.01 (1 H, dd, $J_{2,3}$ 6.5, $J_{3,5}$ 2.5 Hz, 3-H), 4.54 (1 H, br, C*H*OH), 3.71 (3 H, s, CO_2Me), 3.66 (3 H, s, OMe), 3.30 (1 H, m, 5-H), 2.54 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3.5 Hz, 6-H), 2.09 (1 H, d, $J_{2,3}$ 6.5 Hz, 2-H), 2.3 (1 H, m) and 1.6 (6 H, m) [3 × CH_2 and OH (exchangeable with D_2O)], 1.45 (1 H, dd, J_{gem} 16, $J_{5,6}$ 2.5 Hz, 6-H), and 1.33 (3 H, s, Me); *m/e* (%) 406 (15), 378 (27), 350 (5), 322 (45), and 304 (100) (Found: C, 53.0; H, 5.4. $C_{18}H_{22}FeO_7$ requires C, 53.22; H, 5.46%).

Tricarbonyl[*methyl* 1-(2—5-η-4-*methoxy*-1-*methylcyclohexa*-2,4-*dienyl*)-2-(*methoxymethoxy*)*cyclopentanecarboxylate*]*iron* (19).—The hydroxy-ester (16) was converted quantitatively to its methoxymethyl ether (19) by the method described above for the preparation of compound (11), and was obtained as a pale yellow *crystalline solid*, m.p. 83—84 °C; $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 720, and 1 488 cm^{-1}; δ ($CDCl_3$) 5.01 (1 H, dd, $J_{2,3}$ 6.5, $J_{3,5}$ 2.5 Hz, 3-H), 4.58 (2 H, narrow AB q, OCH_2O), 4.35 (1 H, m, C*H*–O), 3.70 (3 H, s, CO_2Me), 3.65 (3 H, s, 4-OMe), 3.36 (3 H, s, OMe), 3.28 (1 H, m, 5-H), 2.57 (1 H, dd, J_{gem} 17, $J_{5,6}$ 3 Hz, 6-H), 2.06 (1 H, d, $J_{2,3}$ 6.5 Hz, 2-H), 2.3 (1 H, m), and 1.9—1.3 (6 H, 3 × CH_2), 1.42 (1 H, dd, J_{gem} 17, $J_{5,6}$ 3 Hz), and 1.27 (3 H, s, Me); *m/e* (%) 450 (5), 422 (35), 366 (60), and 304 (100) (Found: C, 53.7; H, 5.8. $C_{20}H_{26}FeO_8$ requires C, 53.35; H, 5.82).

Tricarbonyl[1-*hydroxymethyl*-1-(2—5-η-4-*methoxy*-1-*methylcyclohexa*-2,4-*dienyl*)-2-(*methoxymethoxy*)*cyclopentane*]-*iron* (20).—To a stirred solution of the ester (19) (2.14 g) in dry tetrahydrofuran (50 ml) under nitrogen at 0 °C was added di-isobutylaluminium hydride (13 ml, 1M in hexane), and the mixture was stirred overnight, warming to room temperature. The aluminium complex was destroyed by addition of methanol (10 ml) and water (10 ml) followed by stirring for 30 min. The mixture was filtered through Celite, the pad washed well with ether (200 ml), and the filtrate washed with water, dried ($MgSO_4$), and evaporated to give the complex (20) as a pale yellow *crystalline solid*, m.p. 116—118 °C (1.80 g, 98%); $\nu_{max.}$ ($CHCl_3$) 3 635, 3 450, 2 048, 1 972, and 1 488 cm^{-1}; δ ($CDCl_3$) 4.97 (1 H, dd, $J_{2,3}$ 6.5, $J_{3,5}$ 2.5 Hz, 3-H), 4.56 (2 H, narrow AB q, OCH_2O), 3.81 (1 H, m, C*H*O), 3.62 (3 H, s, 4-OMe), 3.54 (2 H, br m, CH_2OH), 3.36 (3 H, s, OMe), 3.28 (1 H, m, 5-H), 2.69 (1 H, d, $J_{2,3}$ 6.5 Hz, 2-H), 2.29 (1 H, dd, J_{gem} 16, $J_{5,6}$ 2.5 Hz, 6-H), 1.9–1.3 (8 H, 3 × CH_2, 6-H, and OH), and 1.28 (3 H, s, Me); *m/e* (%) 422 (8), 394 (15), 366 (2), and 338 (100) (Found: C, 53.85; H, 5.95. $C_{19}H_{26}FeO_7$ requires C, 54.05; H, 6.21%).

Tricarbonyl[1-*methoxymethyl*-1-(2—5-η-4-*methoxy*-1-*methylcyclohexa*-2,4-*dienyl*)-2-(*methoxymethoxy*)*cyclopentane*]-*iron* (21).—Sodium hydride (0.70 g, 50% dispersion in mineral oil) was washed under nitrogen with dry pentane, and dry tetrahydrofuran (10 ml), followed by a solution of the complex (20) (1.8 g) in tetrahydrofuran (15 ml), were added. To the stirred mixture at 0 °C was added methyl iodide (7 ml) and stirring was continued for 36 h at room temperature. Excess of sodium hydride was destroyed by careful addition of methanol and the product was extracted in the usual way to give the methyl ether (21) as a *yellow oil*, spectroscopically and chromatographically pure (1.88 g, 100%); $\nu_{max.}$ ($CHCl_3$) 2 045, 1 975, and 1 487 cm^{-1}; δ ($CDCl_3$) 4.97 (1 H, dd, $J_{2,3}$ 6.5, $J_{3,5}$ 2.5 Hz, 3-H), 4.56 (2 H, close AB q, OCH_2O), 3.86 (1 H, m, C*H*O), 3.64 (3 H, s, 4-OMe), 3.36 (3 H, s, OCH_2OMe), 3.34 and 3.08 (each 1 H, d, J_{AB} 10.5 Hz, CH_2O), 3.29 (3 H, s, OMe), 3.29 (1 H, m, obscured, 5-H), 2.65 (1 H, d, $J_{2,3}$ 6.5 Hz, 2-H), 2.32 (1 H, dd, J_{gem} 16, $J_{5,6}$ 2.5 Hz, 6-H), 1.9—1.3 (6 H, 3 × CH_2), 1.45 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, 6-H), and 1.26 (3 H, s, Me); *m/e* (%) 436 (1), 408 (15), 380 (1), and 352 (100) (Found: M^+, 436.116. $C_{20}H_{28}FeO_7$ requires M, 436.1185).

Tricarbonyl[2-*hydroxy*-1-*methoxymethyl*-1-(2—5-η-4-*methoxy*-1-*methylcyclohexa*-2,4-*dienyl*)*cyclopentane*]*iron* (22). —The above complex (21) (1.88 g) was stirred in methanol at 55 °C under nitrogen with toluene-4-sulphonic acid (1.6 g) for 4 h, when t.l.c. examination indicated complete reaction. The usual extractive work-up gave the product (22) as a *yellow syrup*, chromatographically pure (1.40 g, 83%); $\nu_{max.}$ ($CHCl_3$) 3 620, 3 600—3 300, 2 050, 1 975, and 1 488 cm^{-1}; δ ($CDCl_3$) 4.99 (1 H, dd, $J_{2,3}$ 6.5, $J_{3,5}$ 2.5 Hz, 3-H), 4.13 (1 H, br, C*H*O), 3.66 (3 H, s, 4-OMe), 3.36 and 3.10 (each 1 H, d, J_{AB} 10 Hz, CH_2O), 3.33 (1 H, m, 5-H), 3.31 (3 H, s, OMe), 2.65 (1 H, d, $J_{2,3}$ 6.5 Hz, 2-H), 2.34 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, 6-H), 1.9—1.3 (6 H, 3 × CH_2), 1.48 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, 6-H), and 1.34 (3 H, s, Me); *m/e* (%) 364 (50, $M^+ - CO$), 336 (25), and 308 (100) [Found: $M^+ - CO$ 364.1006. $C_{17}H_{24}FeO_5$ ($M - CO$) requires 364.0973].

Cyclisations with Thallium(III) *Trifluoroacetate*.—*Tricarbonyl*[1—4-η-(4*a*β,5*a*β,6,7,8,9,9*a*,9*b*-*octahydro*-3-*methoxy*-9*a*α-*methoxycarbonyl*-9*b*β-*methyldibenzofuran*)]*iron* (13). The hydroxy-ester (7) (0.446 g) was stirred in dry ethanol (10 ml) at 0 °C. Solid sodium hydrogencarbonate (0.3 g) followed by thallium(III) trifluoroacetate (1.2 g) were added and the mixture was stirred for 15 min, after which time a further quantity of $NaHCO_3$ (0.3 g) and TTFA (1.2 g) were added. After 15 min an excess of aqueous sodium carbonate was added, followed by ethyl acetate, and the thallium residues were removed by filtration through Celite. The pad was washed with ethyl acetate and the combined organic extracts were washed with water, dried ($MgSO_4$), and evaporated to give the crude produce (0.20 g). Preparative layer chromatography (SiO_2, 10% EtOAc–benzene) afforded the cyclised product (0.15 g) and a minor amount of recovered hydroxy-ester (0.04 g) (yield based on recovered starting material, 37%). A number of attempts to improve the yield met with no success. The *product* (13) had m.p. 203—205 °C (sublimes); $\nu_{max.}$ 2 055, 1 983, 1 727, and 1 490 cm^{-1}; δ ($CDCl_3$) 4.95 (1 H, dd, $J_{1,2}$ 6, $J_{2,4}$ 2.5 Hz, 2-H), 3.85 (1 H, d, *J* 3.5 Hz, 4a-H), 3.75 (3 H, s, CO_2Me), 3.65 (3 H, s, OMe), 3.50 (1 H, dd, *J* 10, 4.5 Hz, 5a-H), 3.20 (1 H, dd, *J* 3.5, 2.5 Hz, 4-H), 2.30 (1 H, d, *J* 6 Hz, 1-H), 2.3—1.0 (8 H, 4 × CH_2), and 1.18 (3 H, s, Me); *m/e* (%) 418 (12), 390 (40), 362 (5), and 344 (100) (Found: C, 54.25; H, 5.35. $C_{19}H_{22}FeO_7$ requires C, 54.56; H, 5.30%).

Tricarbonyl[1—4-η-(4*a*β,5*a*α,6,7,8,9,9*a*,9*b*-*octahydro*-3-*methoxy*-9*a*β-*methoxycarbonyl*-9*b*β-*methyldibenzofuran*)]*iron* (14). The hydroxy-ester complex (8) (0.100 g) was treated with TTFA–$NaHCO_3$ as above and gave the cyclised product (14) (32 mg, 32%) as a pale yellow *crystalline solid*; $\nu_{max.}$ ($CHCl_3$) 2 055, 1 975, and 1 490 cm^{-1}; δ ($CDCl_3$) 5.25 (1 H, dd, *J* 6, 2.5 Hz, 2-H), 4.10 (1 H, d, *J* 3.5 Hz, 4a-H), 3.66 (3 H, s, CO_2Me), 3.60 (3 H, s, OMe), 3.5 (1 H, obscured, 5a-H), 3.18 (1 H, dd, *J* 3.5, 2.5 Hz, 4-H), 2.15 (1 H, d, *J* 6 Hz, 1-H), 2.1—1.2 (8 H, 4 × CH_2), and 1.14 (3 H, s, Me) (Found: C, 54.5; H, 5.05. $C_{19}H_{22}FeO_7$ requires C, 54.56; H, 5.30%).

Cyclisations with Iron(III) *Chloride on Silica Gel*.—The procedure is described for the cyclisation of hydroxy-ester (7), the others being conducted in an identical manner. Hydrated iron(III) chloride (6.0 g) was dissolved in the minimum volume of diethyl ether, and thoroughly mixed with silica gel (60 g, Merck Kieselgel 60, 70—230 mesh) by shaking. The solvent was removed on the rotary evaporator and the resulting mix was placed under high vacuum (0.01 mmHg) at 80—90 °C for 6 h, when a greenish mix was obtained. The hydroxy-ester (0.60 g) in dry tetrahydrofuran (20 ml) was added to the cooled mix in portions, shaking thoroughly after each addition, and the mixture was evacuated at room temperature for 45 min. The silica reaction mixture was poured onto a column of basic alumina (50 g, Woelm B, activity 1) and the products eluted with ethyl acetate to give a 1 : 1 mixture of products (13) and (14) (0.54 g, 90%), which was used without further purification for the subsequent steps.

The hydroxy-ester complex (16) (0.120 g) gave *tricarbonyl*{5—8-η-(2,3,3*a*α,4*a*β,8*a*,8*b*-*hexahydro*-6-*methoxy*-8*b*α-*methoxycarbonyl*-8*a*β-*methyl*-1H-*cyclopenta*[b]*benzofuran*)}*iron* (17) (0.11 g, 92%), m.p. 124—125 °C (pentane); $\nu_{max.}$ ($CHCl_3$) 2 040, 1 960, and 1 710 cm^{-1}; δ ($CDCl_3$) 5.06 (1 H, dd, *J* 6.5, 2.5 Hz, 7-H), 4.58 (1 H, m, 3a-H), 4.10 (1 H, d, *J* 4 Hz, 4a-H), 3.72 (3 H, s, CO_2Me), 3.71 (3 H, s, OMe), 3.10 (1 H, dd, *J* 4, 2.5 Hz, 5-H), 2.21 (1 H, d, *J* 6.5 Hz, 8-H), 2.0—1.5 (6 H, m, 3 × CH_2), and 1.34 (3 H, s, Me); *m/e* 404 (M^+) (Found: C, 53.3; H, 5.2. $C_{18}H_{20}FeO_7$ requires C, 53.49; H, 4.99%).

The mono-protected diol complex (22) (0.290 g) gave *tricarbonyl*{5—8-η-(2,3,3*a*α,4*a*β,8*a*,8*b*-*hexahydro*-6-*methoxy*-8*b*α-*methoxymethyl*-8*a*β-*methyl*-1H-*cyclopenta*[b]*benzofuran*)}-*iron* (23) (0.237 g, 82%), m.p. 121—122 °C (pentane); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, and 1 490 cm^{-1}; δ ($CDCl_3$) 5.37 (1 H, dd, *J* 6.5, 2.5 Hz, 7-H), 4.15 (1 H, dd, *J* 4, 0.7 Hz, 3b-H), 3.86 (1 H, br s, 3a-H), 3.76 (3 H, s, 6-OMe), 3.59 and 3.12 (each 1 H, d, J_{AB} 9.0 Hz, CH_2OMe), 3.37 (3 H, s, OMe), 3.22 (1 H, dd, *J* 4, 2.5 Hz, 5-H), 2.54 (1 H, dd, *J* 6.5, 0.7 Hz, 8-H), 1.77 (6 H, br s, 3 × CH_2), and 1.35 (3 H, s, Me); *m/e* (%) 390 (20), 362 (70), 334 (20), 306 (70), and 274 (100) (Found: C, 55.15; H, 5.75. $C_{18}H_{24}FeO_6$ requires C, 55.40; H, 5.68%).

Preparation of Dienylium–$Fe(CO)_3$ *Salts*.—*Tricarbonyl*[1—5-η-6-exo$_{Fe}$-(2-*acetoxy*-1-*methoxycarbonylcyclohexyl*)-3-*methoxy*-6-endo$_{Fe}$-*methylcyclohexadienylium*]*iron tetrafluoroborate* (24). Tetrafluoroboric acid (1 ml, 40% aqueous) was added dropwise to stirred acetic anhydride (10 ml) at 0 °C. The mixture was allowed to attain room temperature and the crude mixture of cyclised products (13) and (14) from above (0.54 g) in dichloromethane (10 ml) was added dropwise. Stirring was continued under nitrogen for 30 min, the mixture was poured into stirred diethyl ether, and the product was removed by filtration and washed with ether to give the *tetrafluoroborate* (24) (0.52 g, 73%); $\nu_{max.}$ (Nujol) 2 125, 2 095, 2 070, 1 743, 1 717, and 1 537 cm^{-1}; δ (CD_3CN) 5.83 (2 H, ABX, 5 peaks, $J_{1,2} = J_{4,5} = 7$, $J_{2,4}$ 2.5 Hz, 2-H, 4-H), 4.43 (1 H, dd, *J* 10, 4 Hz, C*H*OAc), 4.06 (3 H, s, OMe), 4.04 and 3.60 (each 1 H, dd, *J* 7, 2 Hz, 1-H and 5-H), 3.72 (3 H, s, CO_2Me), 2.03 (3 H, s, OAc), 1.73 (3 H, s, Me), and 1.9—1.0 (8 H, 4 × CH_2) (Found: C, 45.7; H, 4.8. $C_{21}H_{25}BF_4FeO_8$ requires C, 46.04; H, 4.60%).

Tricarbonyl[1—5-η-6-exo$_{Fe}$-(2-*acetylacetoxy*-1-*methoxycarbonylcyclohexyl*)-3-*methoxy*-6-endo$_{Fe}$-*methylcyclohexadienylium*]*iron hexafluorophosphate* (28). The cyclisation products (13) and (14) (0.137 g) were dissolved in dichloromethane (10 ml) and a solution of keten dimer (2 ml, 50% in acetone) followed by 40% aqueous tetrafluoroboric acid (0.1 ml) were added. The mixture was refluxed gently under nitrogen for 2 h, the solvent removed *in vacuo*, and the residual oily salts taken up in water. The water layer was extracted with ether to remove organic material and ammonium hexafluorophosphate (0.1 g) was added. The salts were extracted into dichloromethane (4 × 2 ml), precipitated with ether, collected by filtration, washed with ether, and dried *in vacuo* to yield the pale yellow *hexafluorophosphate* (28) (0.171 g, 81%); $\nu_{max.}$ (Nujol) 2 120, 2 110,

2 090, 2 065, 2 050, 1 757, 1 750, 1 713, and 1 545 cm^{-1}; $\nu_{max.}$ (MeCN) 2 115, 2 070, 1 748, 1 718, and 1 538 cm^{-1}; δ (CD_3CN) 5.83 and 5.72 (each 1 H, dd, ABX, $J_{2,4}$ 2.0, $J_{1,2} = J_{4,5} = 7.0$ Hz, 2-H and 4-H), 4.67 (1 H, dd, broadened by virtual coupling, J 9, 3 Hz, C*H*OAc), 4.06 (3 H, s, MeO), 4.04 (1 H, dd, obscured) and 3.63 (1 H, dd, J 7, 2.5 Hz, 1-H and 5-H), 3.70 (3 H, s, CO_2Me), 3.53 (2 H, s, CH_2 acetoacetate), 2.21 (3 H, s, OAc), 1.75 (3 H, s, Me), and 1.9—1.0 (8 H, 4 × CH_2) (Found: C, 42.7; H, 4.2. $C_{23}H_{27}F_6FeO_9P$ requires C, 42.61; H, 4.20%).

Tricarbonyl[1—5-η-6-exo$_{Fe}$-(2-*acetoxy*-1-*methoxycarbonylcyclopentyl*)-3-*methoxy*-6-endo$_{Fe}$-*methylcyclohexadienylium*]*iron tetrafluoroborate* (30). The complex (17) (0.12 g) was treated as above with HBF_4–acetic anhydride to give the *tetrafluoroborate* (30) (0.13 g, 82%); $\nu_{max.}$ (Nujol) 2 115, 2 070, 2 050, 1 742, 1 727, and 1 537 cm^{-1}; δ (CD_3CN) 5.95 and 5.80 (each 1 H, dd, J 7, 2 Hz, 2-H and 4-H), 5.33 (1 H, d, J 6 Hz, C*H*OAc), 4.10 (3 H, s, OMe), 3.93 and 3.65 (each 1 H, dd, J 7, 2 Hz, 1-H and 5-H), 3.66 (3 H, s, CO_2Me), 2.0 (3 H, s, OAc), 1.65 (3 H, s, Me), and 1.8—1.2 (6 H, 3 × CH_2) (Found: C, 44.75; H, 4.35. $C_{20}H_{23}BF_4FeO_8$ requires C, 44.98; H, 4.34%).

Tricarbonyl[1—5-η-6-exo$_{Fe}$-(2-*acetoxy*-1-*methoxymethylcyclopentyl*)-3-*methoxy*-6-endo$_{Fe}$-*methylcyclohexadienylium*]-*iron tetrafluoroborate* (31). Treatment of the complex (23) (0.237 g) as above gave the *tetrafluoroborate* (31) (0.260 g, 82%); $\nu_{max.}$ (Nujol) 2 115, 2 060, 1 745, and 1 540 cm^{-1}; δ (CD_3CN) 5.90 and 5.68 (each 1 H, dd, ABX, J 7, 2 Hz, 2-H and 4-H), 4.77 (1 H, d, J 6 Hz, C*H*OAc), 4.07 (3 H, s, OMe), 3.82 centred (2 H, 5-peak ABX, J 7, 2 Hz, 1-H and 5-H), 3.20 (3 H, s, OMe), 3.04 (2 H, s, CH_2OMe), 1.97 (3 H, s, OAc), 1.74 (3 H, s, Me), and 1.8—1.2 (6 H, 3 × CH_2) (Found: C, 45.95; H, 4.65. $C_{20}H_{25}BF_4FeO_7$ requires C, 46.19; H, 4.85%).

Reactions of Dienylium Salts.—(a) *With Cerium*(IV) *Ammonium Nitrate.* The procedure is described for (23), that for the other complexes being identical. The tetrafluoroborate (0.200 g) was stirred in 50% aqueous ethanol (4 ml) at room temperature, and cerium(IV) ammonium nitrate (1.5 g) was added in portions over 40 min. The mixture was poured into water, filtered through Celite, and the pad washed with ether. The aqueous layer was extracted with ether, the combined extracts washed with water, dried ($MgSO_4$), evaporated and chromatographed (silica gel, ether) to give 4-(2-*acetoxy*-1-*methoxycarbonylcyclohexyl*)-4-*methylcyclohexa*-2,5-*dienone* (25) as a colourless crystalline solid, m.p. 101—102 °C (hexane–chloroform), yield 0.076 g (70%); $\nu_{max.}$ (CCl_4) 1 743, 1 725, 1 673, 1 633, and 1 607 cm^{-1}; δ ($CDCl_3$) 7.05 and 6.83 (each 1 H, dd, J 10, 2 Hz, 3-H and 5-H), 6.24 (2 H, d, J 10 Hz, 2-H and 6-H), 4.72 (1 H, dd, J 9, 5 Hz, C*H*OAc), 3.80 (3 H, s, CO_2Me), 1.98 (3 H, s, OAc), 1.30 (3 H, s, Me), and 2.5—1.1 (8 H, 4 × CH_2); *m/e* (%) 306 (2) and 108 (100) (Found: C, 66.4; H, 7.1%; M^+, 306.1455. $C_{17}H_{22}O_5$ requires C, 66.65; H, 7.24%; M, 306.1467).

The tetrafluoroborate (30) (0.120 g) gave 4-(2-*acetoxy*-1-*methoxycarbonylcyclopentyl*)-4-*methylcyclohexa*-2,5-*dienone* (32) (0.063 g, 96%) as colourless crystals, m.p. 69.5—71 °C; $\nu_{max.}$ (CCl_4) 1 742, 1 673, 1 633, and 1 607 cm^{-1}; δ ($CDCl_3$) 7.23 and 7.04 (each 1 H, dd, J 11, 3 Hz, 3-H and 5-H), 6.27 (2 H, d, J 11 Hz, 2-H and 6-H), 5.56 (1 H, br s, C*H*OAc), 3.77 (3 H, s, CO_2Me), 1.97 (3 H, s, OAc), 1.32 (3 H, s, Me), and 2.6—1.6 (6 H, 3 × CH_2) (Found: C, 66.05; H, 6.85%; M^+, 292.1314. $C_{16}H_{20}O_5$ requires C, 65.74; H, 6.90%; M, 292.1311).

The tetrafluoroborate (31) (0.150 g) gave 4-(2-*acetoxy*-1-*methoxymethylcyclopentyl*)-4-*methylcyclohexa*-2,5-*dienone* (33) (0.072 g, 90%) as a colourless oil, chromatographically and spectroscopically pure; $\nu_{max.}$ (CCl_4) 1 745, 1 672, 1 630, and 1 605 cm^{-1}; δ ($CDCl_3$) 7.34 and 7.15 (each 1 H, dd, ABX, J 11, 3 Hz, 3-H and 5-H), 6.22 (2 H, dd, J 11 Hz, 2-H and 5-H), 6.22 (2 H, dd, J 11 Hz, 2-H and 6-H), 5.22 (1 H, dd, J 6, 4 Hz, C*H*OAc), 3.27 (3 H, s, OMe), 3.37 and 3.15 (each 1 H, d, J_{gem} 10 Hz, CH_2OMe), 1.96 (3 H, s, OAc), 1.33 (3 H, s, Me), and 2.4—1.4 (6 H, 3 × CH_2) (Found: M^+, 278.1512. $C_{16}H_{22}O_4$ requires M, 278.1518).

Reaction of Complex (24) *with Dimethyl Sodiomalonate.*—Sodium hydride (50% dispersion in mineral oil, 15 mg, washed with dry pentane) was stirred in dry tetrahydrofuran (1 ml) under nitrogen whilst dimethyl malonate (50 mg) in tetrahydrofuran (1 ml) was added. Stirring was continued at room temperature for 10 min, and the complex (24) (100 mg) was added with back-flushing of nitrogen. The resulting blood-red mixture was stirred at room temperature for 15 min, poured into brine, and extracted with ether. The extracts were washed with 20% aqueous hydrochloric acid, saturated sodium hydrogencarbonate solution, and water, dried ($MgSO_4$), and evaporated to give a yellow oil (65 mg). T.l.c. examination showed three compounds, one of which was unreacted dimethyl malonate. Preparative layer chromatography (silica gel–ether) afforded the dienone (25) (40 mg, 72%) and a yellow oil whose spectral properties were consistent with the *structure* (26) (11 mg, 10%); $\nu_{max.}$ (CCl_4) 2 030, 1 982, 1 738, 1 725, 1 690, and 1 533 cm^{-1}; δ (CD_2Cl_2) 5.23 (1 H, s, malonyl C*H*), 4.95 (2 H, d, J 7 Hz, 2-H, 4-H), 4.55 (1 H, dd, J 9, 5 Hz, C*H*OAc), 3.92 (3 H, s, MeO), 3.63 (3 H, s, CO_2Me), 3.50 (6 H, s, 2 × CO_2Me), 2.57 and 2.30 (each 1 H, dd, J 7, 2.5 Hz, 1-H and 5-H), 1.98 (3 H, s, OAc), 1.60 (3 H, s, Me), and 1.9—1.0 (8 H, 4 × CH_2); *m/e* 592 (M^+).

Reaction of (31) *with Sodiomalononitrile.*—Sodiomalononitrile was prepared in tetrahydrofuran as above from sodium hydride (10 mg, 50% in mineral oil) and malononitrile (25 mg). The tetrafluoroborate (25 mg) was added, and the mixture was stirred for 15 min and worked up as above to give the dienone (33) (10 mg) identical to that prepared by reaction of (31) with Ce^{IV}. No other products were observed.

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REFERENCES

[1] Part 12, A. J. Pearson and M. Chandler, *Tetrahedron Lett.*, 1980, **21**, 3933.
[2] (*a*) A. J. Pearson, *J. Chem. Soc., Chem. Commun.*, 1980, 488; (*b*) C. W. Ong and A. J. Pearson, *Tetrahedron Lett.*, 1980, **21**, 2349.
[3] See *e.g.* A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1882.
[4] R. E. Ireland, G. G. Brown, jun., R. H. Stanford, jun., and T. C. McKenzie, *J. Org. Chem.*, 1974, **39**, 51.
[5] A. J. Pearson, E. Mincione, M. Chandler, and P. R. Raithby, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2774.
[6] T. C. Jempty, L. L. Miller, and Y. Mazur, *J. Org. Chem.*, 1980, **45**, 749.
[7] A. J. Pearson and P. R. Raithby, *J. Chem. Soc., Perkin Trans. 1*, 1980, 395.
[8] A. J. Pearson and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1981, 884.
[9] C. W. Ong, Certificate of Postgraduate Study Dissertation, University of Cambridge, 1980.

[10] See *e.g.* T. V. Harris, J. W. Rathke, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1978, **100**, 6966; M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1963, 189; T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104.
[11] (*a*) E. G. Bryan, A. L. Burrows, B. F. G. Johnson, J. Lewis, and G. M. Schiavon, *J. Organomet. Chem.*, 1977, **127**, C19; (*b*) R. J. H. Cowles, B. F. G. Johnson, P. L. Josty, and J. Lewis, *Chem. Commun.*, 1969, 392.
[12] D. A. Brown, S. K. Chawla, and W. K. Glass, *Inorg. Chim. Acta*, 1976, **19**, L31.
[13] A. J. Pearson, *J. Chem. Soc., Perkin Trans. 1*, 1980, 400.
[14] A. J. Pearson and M. Chandler, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2238.
[15] See *e.g.* E. J. Corey, E. J. Trybulski, L. S. Melvin, K. C. Nicolaou, J. A. Secrist, R. Lett, P. W. Sheldrake, J. R. Falck, D. J. Brunelle, M. F. Haslanger, S. Kim, and S. Yoo, *J. Am. Chem. Soc.*, 1978, **100**, 4618, and references cited therein.
[16] S. Danishefsky, C. F. Yan, R. K. Singh, R. B. Gammill, P. M. McCurry, jun., N. Fritsch, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 7001; S. Danishefsky, T. Harayama, and R. K. Singh, *ibid.*, 1979, **101**, 7008; W. Gramlich and H. Plieninger, *Chem. Ber.*, 1979, **112** 1571; H. Plieninger and W. Gramlich, *ibid.*, 1978, **111**, 1944.