Organoiron Complexes in Organic Synthesis. Part 5.[1] Spirocyclisation Reactions of Tricarbonylcyclohexadienyliumiron Complexes

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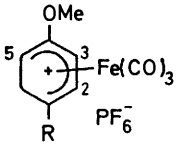
Attempted spirocyclisation of tricarbonyl{dimethyl[3-(4-methoxycyclohexa-2,4-dienylium)propyl]malonate}iron hexafluorophosphate (4) and tricarbonyl[methyl 5-(4-methoxycyclohexa-2,4-dienylium)-3-oxopentanoate]iron hexafluorophosphate (11) to the desired spiro[4.5]decane derivatives (5) and (12) failed under a variety of mild conditions. Spirocyclisation of tricarbonyl[methyl 6-(4-methoxycyclohexa-2,4-dienylium)-3-oxohexanoate]-iron hexafluorophosphate (25) occurs smoothly and rapidly at −78° to give the tricarbonyl[η-7—10-(methyl 9-methoxy-2-oxospiro[5.5]undeca-7,9-diene-1-carboxylate)]iron diastereoisomers (26) and (27).

PART 3 [2] described a successful new approach to the synthesis of spiro[4.5]decane and spiro[5.5]undecane derivatives, utilising the ability of a 4-methoxy-substituent in cyclohexadienylium complexes (1a and b) to direct the dimethylmalonyl carbanion into the substituted 1-position. Before utilising this approach for



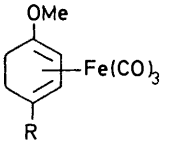
(1)

a; R = $[CH_2]_2CO_2Me$
b; R = $[CH_2]_3CO_2Me$
c; R = H
d; R = $[CH_2]_4CO_2Me$
e; R = $[CH_2]_2COMe$

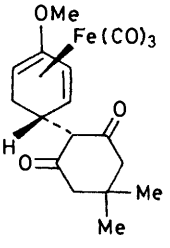
synthesis of natural spirocycles we decided to investigate a possible alternative method *via* intramolecular reaction of a 1,3-dicarbonyl group contained in the substituent R, as in salts (4), (11), and (25), which might lead to spirocyclisation. Neither this type of reaction, nor the synthesis of cyclohexadienylium complexes with this degree of functionality, have been previously attempted. Apart from the intrinsic value of extending organic synthetic methods to complexed ligands and determining the combined behaviour of the groups present, we also wished to assess the feasibility of the proposed cyclisations prior to embarking on a number of projects aimed towards diterpenoid synthesis. We could then decide on whether the carbanion addition approach previously described [2-4] is the most useful.

RESULTS AND DISCUSSION

Attempted Formation of Spiro[4.5]decane Derivatives.—As starting materials we required complexes containing either a *gem*-diester or β-keto-ester in the C-1 substituent, and whilst the introduction of such groupings is readily achieved for organic molecules by Corey's method,[5] using dimethyl carbonate and sodium hydride on a monoester or ketone, this type of reaction has not been previously attempted with iron carbonyl derivatives. In general metal carbonyls are sensitive to metal hydrides,[6] although diene–$Fe(CO)_3$ complexes have been found to be fairly stable to lithium aluminium hydride and sodium borohydride.[7] We first chose to investigate this reaction with the pentanoic ester derivatives (2), readily prepared as previously described for the lower homologues,[2] and were gratified to find that the monoester underwent smooth conversion to the *gem*-diester (3) at elevated temperatures. Hydride abstraction gave, after treatment with aqueous ammonium hexafluorophosphate, the stable crystalline salt (4). It is known [8] that tricarbonyl(cyclohexadienylium)iron salts such as (1c) will react with 1,3-dicarbonyl compounds, such as dimedone, in boiling ethanol to give products of alkylation such as (15). Similar treatment of the *gem*-diester (4) gave no cyclisation to (5), but resulted in loss of the acidic exocyclic methylene proton α to the dienylium terminus C-1, to give the triene complex (6) together with transesterification products (Scheme 1). Treatment of (4) under mild conditions with a variety of bases again resulted only in formation of (6), recognised by its n.m.r., i.r., and mass spectra by comparison with similar previously isolated



(2) R = $[CH_2]_4CO_2Me$
(3) R = $[CH_2]_3CH(CO_2Me)_2$
(7) R = $[CH_2]_2CO_2Me$
(8) R = $[CH_2]_2CO_2H$
(9) R = $[CH_2]_2CO{\cdot}Me$
(10) R = $[CH_2]_2CO{\cdot}CH_2{\cdot}CO_2Me$
(21) R = $[CH_2]_3CO_2Me$
(22) R = $[CH_2]_3CO_2H$
(23) R = $[CH_2]_3CO{\cdot}Me$
(24) R = $[CH_2]_3CO{\cdot}CH_2{\cdot}CO_2{\cdot}Me$



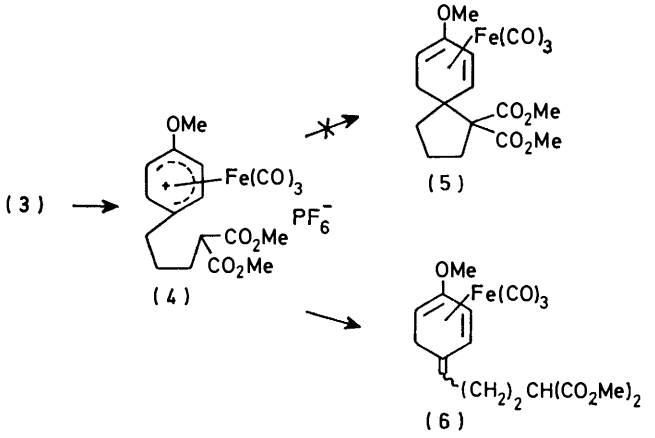
(15)

complexes.[4] Thus, the olefinic region of the n.m.r. spectrum showed two protons, corresponding to 3-H and the exocyclic vinyl proton (of unknown geometry, the broad signal indicating a mixture of double-bond isomers) whilst the methoxy-singlet occurred at δ 3.63, the characteristic position for this type of compound.[2-4,9]

Alkylation of 1,3-dicarbonyl compounds with, for

example, sterically hindered alkyl halides has been achieved using Lewis acid catalysis,[10] and we imagined that this might overcome the above base-catalysed deprotonation problem. However, treatment of (4) with a slight excess of aluminium chloride at ambient temperature led only to (6) and aromatic material (n.m.r.), which arises by loss of $Fe(CO)_3$ from (6) (which is very unstable).

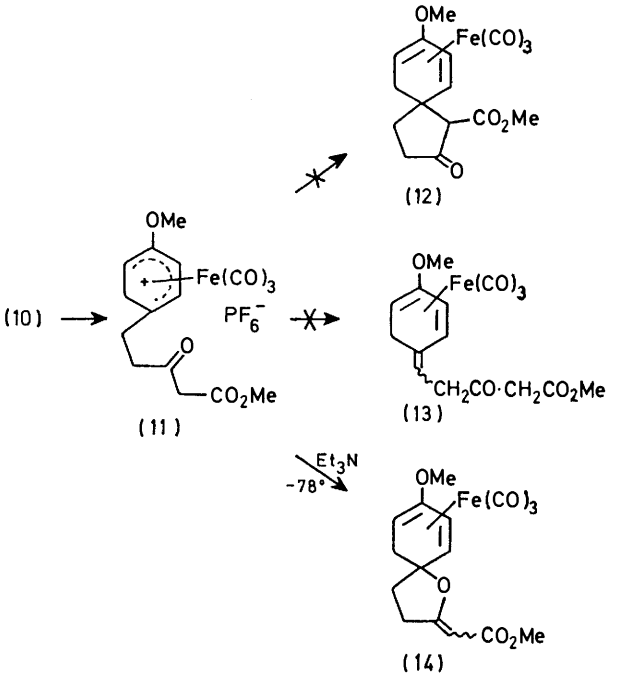
We next chose to study the behaviour of the β-keto-ester derivative (11) which was readily synthesised as a stable yellow crystalline hexafluorophosphate (Experimental). [We were unable to obtain (9) directly from the uncomplexed ketone.] It seemed likely that the keto-ester methylene protons might be significantly more acidic than those flanked by two ester groups such as in (4) and therefore deprotonate preferentially at this site. This was indeed the case, although the subsequent reaction did not proceed in the desired manner. Treatment of (11) with triethylamine in dichloromethane



SCHEME 1

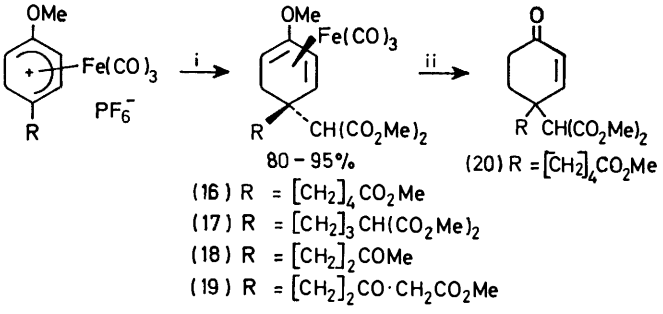
solution at −78° gave an unstable oil, t.l.c. of which showed two overlapping spots. The i.r. spectrum showed no cyclopentanone absorption, ruling out structure (12), and complete loss of the typical β-keto-ester absorptions at 1 745 and 1 720 cm^{-1}, to be replaced by two new bands at 1 702 and 1 645 cm^{-1}. Absence of the typical C=C absorption at *ca.* 1 610 cm^{-1} ruled out structure (13), though the n.m.r. spectrum showed two vinyl protons and the remaining signals expected for this type of compound. On the basis of these data we have assigned structure (14) (mixture of double-bond isomers) to this product (conjugated ester and enol ether groupings), which therefore arises by intramolecular *O*-alkylation of the keto-ester (Scheme 2). Since for present purposes this was an undesired reaction, and since the same product was obtained using a variety of mild bases and solvents, this was not pursued further. Attempted removal of $Fe(CO)_3$, using trimethylamine oxide in benzene at 50 °C gave aromatic material, due to facile opening of the furanoid ring.

The salts (4), (11), and (1d and e) [the latter two prepared by hydride abstraction from (2) and (9)] all reacted in the normal manner with sodio-dimethylmalonate (Scheme 3), thus complementing our previous work on the synthesis of highly functionalised 4,4-disubstituted cyclohexenones. Removal of iron can be readily effected by treatment with trimethylamine



SCHEME 2

oxide,[11] and in this present series we looked at the use of ethanolic copper(II) chloride,[12] which converted the triester complex (16) to the cyclohexenone (20) in a single step.

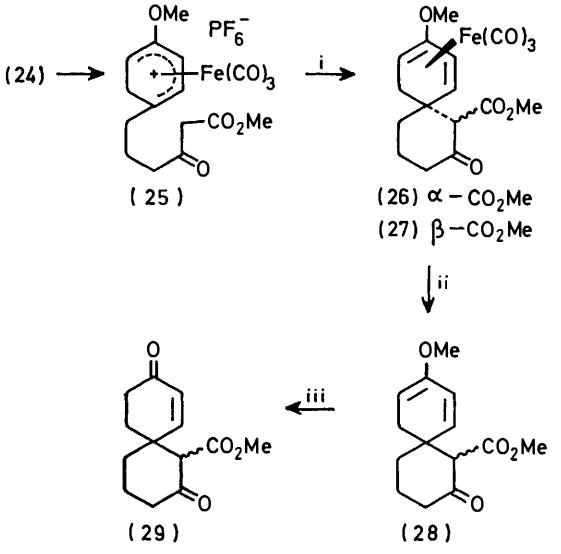


SCHEME 3 Reagents: i, $NaCH(CO_2Me)_2$–THF at −78 °C; ii, $CuCl_2$–EtOH

Synthesis of Spiro[5.5]*undecane Derivatives* (*Scheme* 4). —Encouraged by the above selectivity for proton removal from the β-keto-ester group of (11) we decided to investigate the behaviour of the next higher homologue (25), which was readily obtained (as a gum which could not be crystallised) by a similar series of transformations (Experimental). Our optimism was amply rewarded when treatment of a methylene chloride solution of (25) with triethylamine at −78° for *ca.* 15 min gave a crystalline crude product in very high yield, t.l.c. examination of which showed two closely running major components and a less polar minor component. Prepara-

tive layer chromatography gave an almost negligible amount (4—5 mg) of the latter compound which was not characterised, but is most likely the homologue of (13). Extraction of the two more polar bands led to crystalline compounds having n.m.r. spectra identical to each other and to the crude product. The spectral data were consistent with a mixture of complexes (26) and (27) which, being diastereoisomers having a labile proton at the epimeric centre, are readily interconvertible (*e.g.* on silica gel). Their separation was not further attempted. Treatment of the mixture with trimethylamine oxide gave (28), which could be hydrolysed to the spirocyclic enone derivative (29).

Conclusions.—The reactions described above for complexes (11) and (25) can be rationalised on the basis of Baldwin's rules for ring closure.[13] Thus, cyclisation of (11) by intramolecular *C*-alkylation of the β-keto-ester enolate corresponds to a disfavoured 5-*endo*-trigonal



SCHEME 4 Reagents: i, Et_3N at −78 °C; ii, Me_3NO; iii, H_3O^+

process. The preferred *O*-alkylation observed with this molecule is sterically less difficult, and compares well with the γ-bromoketone enolate reactions investigated by Baldwin.[13b] On the other hand, cyclisation onto carbon is a favoured 6-*endo*-trigonal process for (25), and occurs readily. Reactions of these complexes are, however, less simple than with many organic molecules, as illustrated by the behaviour of (4). Cyclisation of the enolate from this diester would be a 5-*exo*-trigonal process, which is normally favoured (hence the reason for studying this molecule first). In the case of (4) we observe that the diester methine proton is insufficiently acidic, compared to the exocyclic methylene protons α to the dienylium terminus, with the result that base treatment leads to preferential loss of the latter.

We are continuing to investigate the potential of this cyclisation process and its application to the synthesis of pharmacologically interesting molecules.

EXPERIMENTAL

I.r. spectra were determined with Perkin-Elmer 457 or 577, mass spectra with A.E.I. MS12 (organometallics) or MS30 (organic compounds), and ^1H n.m.r. spectra in deuteriochloroform unless otherwise stated with Perkin-Elmer R12 (60 MHz) or Varian HA100 (100 MHz) instruments. M.p.s are uncorrected. All chromatographic operations with iron complexes were conducted under nitrogen.

Tricarbonyl[methyl 5-(4-methoxycyclohexa-1,3-dienyl)pentanoate]iron (2).—Friedel–Crafts acylation of anisole with glutaric anhydride and aluminium chloride in dichloromethane, followed by Clemmensen reduction gave 5-(4-methoxyphenyl)pentanoic acid. Birch reduction of this compound (41 g) in ammonia (1.0 l) containing t-butyl alcohol (50 ml) with lithium metal (16 g) and maintaining a permanent blue colour for 10 h, followed by work-up as previously described [2] afforded the corresponding dihydroderivative (36 g), $\nu_{max.}$ (Nujol) 1 712, 1 668, and 1 610 cm^{-1}; δ 11.07 (1 H, CO_2H), 5.37 (1 H) and 4.60 (1 H) (vinyl), 3.52 (3 H, s, OMe), and 2.70 and 2.50—1.40 (12 H total). This compound was unstable and was immediately methylated under nitrogen with dimethyl sulphate (20 ml) in refluxing acetone (500 ml) containing potassium carbonate (40 g) to give the crude ester (36 g) judged to be sufficiently pure for the next stage from its n.m.r. spectrum, $\nu_{max.}$ (film) 1 740, 1 670, and 1 612 cm^{-1}; δ 5.38 (1 H) and 4.60 (1 H) (vinyl), 3.64 (3 H, s, CO_2Me), 3.50 (3 H, s, OMe), and 2.70 and 2.50—1.40 (12 H total). The ester (15.5 g) was stirred with pentacarbonyliron (20 ml) in dibutyl ether (100 ml) under nitrogen at 120—130 °C for 70 h at which time the cooled mixture was filtered through Celite and heated with a further quantity of pentacarbonyliron (10 ml) for a further 70 h, after which time no further change in the i.r. spectrum was apparent. The usual work-up [2] afforded a crude complex (13.4 g) from which unchanged diene was removed by distillation at oil-pump pressure. Chromatography of the residues on silica gel with 5% ethyl acetate in benzene afforded the *complex* (2) (11.0 g, 44%), which could be crystallised from pentane at −40 °C to give yellow crystals, m.p. 26—28 °C, $\nu_{max.}$ ($CHCl_3$) 2 045, 1 960, and 1 730 cm^{-1}; δ 5.15 (1 H, d, $J_{2,3}$ 5 Hz, 2-H), 4.90 (1 H, d, $J_{2,3}$ 5 Hz, 3-H), 3.65 (3 H, s, CO_2Me), 3.41 (3 H, s, OMe), and 2.50—1.50 (12 H total), *m/e* 364 (M^+) (Found: C, 53.04; H, 5.35. $C_{16}H_{20}FeO_6$ requires C, 52.75; H, 5.55%).

Tricarbonyl[methyl 5-(4-methoxycyclohexa-2,4-dienylium)-pentanoate]iron Tetrafluoroborate and Hexafluorophosphate (1d).—The complex (2) (1.0 g) was treated with triphenylmethylium tetrafluoroborate (1.0 g) in refluxing dry dichloromethane (25 ml) under nitrogen for 1 h. The solution was poured into an excess of ' wet ' ether, and after scratching to induce crystallisation the product was removed by filtration and washed thoroughly with ether to give the *tetrafluoroborate* (1d) (1.05 g, 85%), $\nu_{max.}$ (Nujol) 2 115, 2 055, and 1 733 cm^{-1}; δ (CD_3CN) 6.92 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2 Hz, 3-H), 5.60 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), 3.95 (1 H, m, 5-H), 3.80 (3 H, s, OMe), 3.64 (3 H, s, CO_2Me), 3.00 (1 H, dd, J_{gem} 15, $J_{5,6}$ 7 Hz, *endo*-6-H), and 2.50—1.40 (9 H). Since hexafluorophosphates are usually more stable for storage purposes, this compound was converted to its hexafluorophosphate by precipitation from aqueous solution with ammonium hexafluorophosphate, followed by recrystallisation from dichloromethane–ether (recovery 95%) (Found: C, 37.7; H, 3.75. $C_{16}H_{19}F_6FeO_6P$ requires C, 37.8; H, 3.7%).

Tricarbonyl{dimethyl [3-(4-methoxycyclohexa-1,3-dienyl)-propyl]malonate}iron (3).—The monoester (2) (2.0 g) in dry dioxan (8.0 ml) was added slowly (syringe) to a stirred suspension of sodium hydride (from 600 mg dispersion in mineral oil, washed under nitrogen with dry pentane) and dimethyl carbonate (3.5 ml) in dry dioxan (14.0 ml) at room temperature under nitrogen. The mixture was stirred at room temperature for 19 h, then at 80—90 °C for 12 h. The usual work-up,[5] followed by column chromatography on silica gel, afforded (3) as a yellow oil eluted with 10% ethyl acetate in benzene (1.77 g, 76%), $\nu_{max.}$ ($CHCl_3$) 2 050, 1 965, 1 755, and 1 735 cm^{-1}; δ 5.15 (1 H, d, *J* 5 Hz, 2-H), 4.90 (1 H, d, *J* 5 Hz, 3-H), 3.69 (6 H, s, 2 × CO_2Me), 3.40 (3 H, s, OMe), 3.35 (1 H, t, *J* 6 Hz, CH of *gem*-diester), 2.1—1.5 (10 H) (Found: M^+, 422. $C_{18}H_{22}FeO_8$ requires *M*, 422).

Tricarbonyl{dimethyl [3-(4-methoxycyclohexa-2,4-dienylium)propyl]malonate}iron Hexafluorophosphate (4).—Triphenylmethylium tetrafluoroborate (2.5 g) was dissolved in the minimum volume of dry dichloromethane. The diester (3) (1.53 g) dissolved in a similar volume of dichloromethane was added and the darkened mixture allowed to stand under nitrogen at room temperature for 2 h. The mixture was poured into an excess of ether and the tetrafluoroborate salt thoroughly extracted into water. After addition of ammonium hexafluorophosphate (1.0 g) in water (5 ml), the hexafluorophosphate was extracted into dichloromethane. The extract was dried ($MgSO_4$) and the salt precipitated by addition of ether to give the yellow crystalline *hexafluorophosphate* (4) (1.45 g, 71%), $\nu_{max.}$ (Nujol) 2 120, 2 078, 2 055, 1 748, and 1 725 cm^{-1}; δ (CD_3CN) 6.80 (1 H, dd, $J_{2,3}$ 5.5, $J_{3,5}$ 2 Hz, 3-H), 5.58 (1 H, d, $J_{2,3}$ 5.5 Hz, 2-H), 3.9 (1 H, m, 5-H), 3.79 (3 H, s, OMe), 3.70 (6 H, s, 2 × CO_2Me), 3.40 (1 H, t, *J* 7 Hz, CH of *gem*-diester), 2.98 (1 H, dd, J_{gem} 16, $J_{5,6}$ 6 Hz, *endo*-6-H), 2.32 (1 H, d, J_{gem} 16 Hz, *exo*-6-H), and 2.10—1.10 (6 H) (Found: C, 38.15; H, 4.0. $C_{18}H_{21}F_6FeO_8P$ requires C, 38.2; H, 3.75%).

Tricarbonyl[3-(4-methoxycyclohexa-1,3-dienyl)propionic acid]iron (8).—The ester complex (7) (2.0 g) from previous studies [2] was stirred in methanol (150 ml) under nitrogen whilst a solution of potassium hydroxide (8 g) in water (50 ml) was added. The solution was stirred for 4 h at room temperature, poured onto ice–hydrochloric acid, and the complex collected by filtration, washed thoroughly with water, and dried *in vacuo* to give the acid (8) (1.4 g, 73%) which could be recrystallised from dichloromethane by dropwise addition of hexane (1.2 g, 63%), m.p. 120—122 °C, $\nu_{max.}$ (Nujol) 2 050, 1 960, and 1 700 cm^{-1}; δ 9.3br (1 H, CO_2H), 5.18 (1 H, d, $J_{2,3}$ 5 Hz, 2-H), 4.95 (1 H, d, $J_{2,3}$ 5 Hz, 3-H), 3.40 (3 H, s, OMe), and 2.8—1.5 (8 H); *m/e* 322 (M^+) (Found: C, 48.55; H, 4.5. $C_{13}H_{14}FeO_6$ requires C, 48.5; H, 4.5%).

Tricarbonyl[4-(4-methoxycyclohexa-1,3-dienyl)butan-2-one]-iron (9).—The acid (8) (1.05 g) was stirred in dry ether (50 ml) under nitrogen at 0 °C whilst methyl-lithium (4.0 ml of a 1.7M solution in ether) was added dropwise by means of a syringe. The mixture was allowed to warm to room temperature and stirred for a further 4 h, when it was poured into briskly stirred ice-cold 10% aqueous hydrochloric acid. The ether layer was washed with water, saturated sodium carbonate solution, and again with water and dried ($MgSO_4$). Removal of solvent followed by column chromatography on silica gave the ketone (9) as a yellow *solid*, eluted with benzene (0.88 g, 85%), m.p. 24—26 °C, $\nu_{max.}$ ($CHCl_3$) 2 040, 1 960, and 1 714 cm^{-1}; δ 5.18 (1 H, d, $J_{2,3}$ 5 Hz, 2-H), 4.95 (1 H, d, $J_{2,3}$ 5 Hz, 3-H), 3.45 (3 H, s, MeO), 2.16 (3 H, s, COMe), and 2.80—1.50 (8 H); *m/e* 320 (M^+) (Found: C, 52.75; H, 5.25. $C_{14}H_{16}FeO_5$ requires C, 52.5; H, 5.05); 2,4-dinitrophenylhydrazone, m.p. 153.5—155 °C.

Tricarbonyl[4-(4-methoxycyclohexa-2,4-dienylium)butan-2-one]iron Hexafluorophosphate (1e).—The ketone (9) (1.27 g) and triphenylmethylium tetrafluoroborate (1.50 g) were heated at reflux in dry dichloromethane (25 ml) under nitrogen for 1.5 h. The cooled mixture was poured into an excess of ether and the salt extracted with water (3 × 10 ml). To the combined aqueous extracts was added a solution of ammonium hexafluorophosphate (1.0 g) in water (5 ml) and the product was extracted into dichloromethane (2 × 10 ml). The organic extract was dried ($MgSO_4$) and the salts crystallised by slow addition of excess of ether. Filtration, followed by washing with ether and drying *in vacuo* yielded the hexafluorophosphate (1e) as yellow crystals (0.80 g, 43%). Chromatography of the recovered neutral complexes (from ether solution above) gave only 0.10 g (8%) of unchanged starting material. The *product* (1e) gave $\nu_{max.}$ (Nujol) 2 105, 2 060, and 1 716 cm^{-1}; δ (CD_3CN) 6.73 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 3 Hz, 3-H), 5.52 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), 5.82 (1 H, m, 5-H), 3.70 (3 H, s, MeO), 2.91 (1 H, dd, J_{gem} 16, $J_{5,6}$ 6 Hz, *endo*-6-H), 2.0 (3 H, s, COMe), 2.5—1.7 (5 H) (Found: C, 36.45; H, 3.5. $C_{14}H_{15}F_6FeO_5P$ requires C, 36.25; H, 3.25%).

Tricarbonyl[methyl 5-(4-methoxycyclohexa-1,3-dienyl)-3-oxopentanoate]iron (10).—The ketone (9) (1.376 g) in dry dioxan (4.0 ml) was added dropwise (syringe) to a stirred suspension of sodium hydride (from 0.50 g dispersion in mineral oil, washed under nitrogen with dry pentane) and dimethyl carbonate (2.2 g) in dry dioxan (8.0 ml). The mixture was stirred at room temperature under nitrogen overnight and then at 70—80 °C for 2 h. Work-up,[5] followed by column chromatography on silica gel, gave the β-keto-ester (10) as a yellow oil, eluted with 10% ethyl acetate in benzene (1.390, 86%, after removal of solvents at 0.005 mmHg), $\nu_{max.}$ ($CHCl_3$) 2 050, 1 960, 1 745, and 1 720 cm^{-1}; δ 5.19 (1 H, d, *J* 5 Hz, 2-H), 4.97 (1 H, d, *J* 5 Hz, 3-H), 3.73 (3 H, s, CO_2Me), 3.47 (2 H, s, keto-ester CH_2), 3.45 (3 H, s, OMe), 2.90—1.50 (8 H) (Found: M^+, 378. $C_{16}H_{18}FeO_7$ requires *M*, 378).

Tricarbonyl[methyl 5-(4-methoxycyclohexa-2,4-dienylium)-3-oxopentanoate]iron Hexafluorophosphate (11).—To a solution of triphenylmethylium tetrafluoroborate (3.0 g) in the minimum volume of dry dichloromethane was added the β-keto-ester (10) (1.39 g) in a similar volume of dichloromethane. The mixture was allowed to stand at room temperature under nitrogen for 1 h. Work-up as for complex (1e) above furnished the hexafluorophosphate (11) as yellow crystals (0.97 g, 51%). Chromatography of the neutral ether extracts gave unchanged starting material (0.30 g, 22%). Prolonged reaction times lead to decomposition and no yield improvement. The complex (11) gave $\nu_{max.}$ (Nujol) 2 120, 2 078, 1 740, and 1 727 cm^{-1}; δ (CD_3CN) 6.79 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 3 Hz, 3-H), 5.61 (1 H, d, *J* 6 Hz, 2-H), 3.91 (1 H, m, 5-H), 3.78 (3 H, s, CO_2Me), 3.66 (3 H, s, OMe), 3.48 (2 H, s, keto-ester CH_2), 2.98 (1 H, dd, J_{gem} 16, $J_{5,6}$ 6 Hz, *endo*-6-H), and 2.80—2.10 (5 H) (Found: C, 36.85; H, 3.25. $C_{16}H_{17}F_6FeO_7P$ requires C, 36.8; H, 3.3%).

Attempted Cyclisation of (4).—(*a*) *Heating in ethanol.* The complex (4) (0.20 g) and sodium hydrogen carbonate (30 mg; removes HPF_6 formed) were stirred in absolute ethanol (5 ml) under nitrogen and in an oil-bath at 60 °C for 4 h.

The cooled mixture was poured into water and extracted with ether in the usual way to give the crude product as a yellow oil (0.13 g) which was a single spot on t.l.c. Examination of the n.m.r. spectrum showed the presence of complex (6), together with products of transesterification (mixture of ethyl and methyl esters). Spectral data for (6) are given later. Similar results were given by (11). Removal of iron with an excess of trimethylamine *N*-oxide in refluxing benzene [3,11] gave only aromatic products from both these compounds.

(b) *Tetramethylammonium acetate.* To a stirred solution of the hexafluorophosphate (4) (0.30 g) in dry acetonitrile (6 ml) at −30 °C under nitrogen was added dropwise (syringe) a solution of tetramethylammonium acetate (0.08 g) in dry acetonitrile (4 ml). Stirring was continued for 6 h, whilst the cooling bath was allowed to reach room temperature, and the solution was poured into water (50 ml) and quickly extracted with ether. The combined extracts were washed with water and dried ($MgSO_4$). Removal of solvent under vacuum at room temperature (15 mmHg, then 0.05 mmHg) gave a yellow oil which was a single spot on t.l.c. (0.18 g, 83%), the n.m.r. spectrum showing >95% pure complex (6), $\nu_{max.}$ ($CHCl_3$) 2 060, 1 975, 1 750sh, 1 738, and 1 610 cm^{-1}; δ 5.13 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 3 Hz, 3-H), 4.9—4.5 (1 H, m, exocyclic vinyl, two isomers), 3.72 (6 H, s, 2 × CO_2Me), 3.63 (3 H, s, OMe), 3.33 (1 H, d, $J_{2,3}$ 7 Hz, 2-H), 3.60—3.30 (2 H, m, 5-H and *gem*-diester CH), and 2.40—1.70 (6 H) (Found: M^+, 420. $C_{18}H_{20}FeO_8$ requires *M*, 420).

(c) *Triethylamine.* A solution of the salt (4) (0.20 g) in dry dichloromethane (10 ml) was stirred under nitrogen at −78 °C whilst a solution of the amine (0.05 g) in dichloromethane (5 ml) was added dropwise (syringe). After 0.5 h at this temperature the mixture was poured into water (150 ml) and extracted with ether in the usual way to give pure (6) (0.07 g).

(d) *Aluminium chloride.* The hexafluorophosphate (4) (0.30 g) in dry nitromethane (5 ml) was added to a stirred suspension of aluminium chloride (0.08 g) in nitromethane (5 ml) under nitrogen. Stirring was continued at room temperature for 19 h, after which the mixture was poured into water (50 ml) and extracted with ether in the usual way to give a crude product (0.09 g), the n.m.r. spectrum of which showed only aromatic compounds together with a minor amount of (6).

Cyclisation of (11).—The hexafluorophosphate (11) (0.25 g) was stirred in dry dichloromethane (20 ml) at −78 °C under nitrogen whilst triethylamine (0.07 g) in dichloromethane (2 ml) was added dropwise. The stirred mixture was maintained at −78 °C for 20 min, then poured into water and extracted with ether in the usual way to give a very unstable yellow oil (0.18 g, 100%) showing two overlapping spots on t.l.c., the n.m.r. and i.r. spectra of which indicated a mixture of isomers (14). This compound was too unstable for preparative t.l.c., $\nu_{max.}$ ($CHCl_3$) 2 060, 1 975, 1 702, and 1 635 cm^{-1}; δ 5.15 (2 H, m, 3-H and exocyclic vinyl), 3.70 (3 H, s, plus 2 H obscured, CO_2Me, CH_2), 3.62 (3 H, s, OMe), 3.50—3.00 (2 H, m), and 2.50—2.10 (4 H, m, 2- and 5-H and 2 × CH_2); *m/e* 376 (M^+). Treatment of this compound with anhydrous trimethylamine *N*-oxide (0.6 g) in benzene (10 ml) at 50 °C for 1 h resulted in the formation of aromatic material. The other cyclisation methods described above for (4) also resulted in the formation of (14).

Reaction of Salts with Sodio-dimethylmalonate.—Reactions were carried out in dry tetrahydrofuran at −78 °C as previously described,[2] the products being as indicated below. Complex (1d) (0.65 g) gave, after purification by preparative layer chromatography, the complex (16) (0.68 g, 95%) as a yellow gum which did not crystallise after prolonged standing at sub-zero temperatures of either a solution in pentane or the compound itself, but which appeared quite pure in the n.m.r. spectrum, $\nu_{max.}$ ($CHCl_3$) 2 058, 1 970, 1 755sh, and 1 730 cm^{-1}; δ 5.0 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 2 Hz, 3-H), 3.72 (3 H, s, CO_2Me), 3.70 (3 H, s, CO_2Me), 3.67 (3 H, s, CO_2Me), 3.62 (3 H, s, OMe), 3.50 (1 H, s, *gem*-diester CH), 3.30 (1 H, m, 5-H), 2.73 (1 H, d, *J* 7 Hz, 2-H), and 2.7—1.2 (10 H) (Found: M^+, 494. $C_{21}H_{26}FeO_{10}$ requires *M*, 494).

Complex (1e) (0.20 g) gave the *complex* (18) (0.175 g, 90%). The crude product crystallised after storing at 0 °C, m.p. 103—105 °C, $\nu_{max.}$ ($CHCl_3$) 2 060, 1 970, 1 760, and 1 730 cm^{-1}; δ 5.0 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 3 Hz, 3-H), 3.75 (3 H, s) and 3.73 (3 H, s) (2 × CO_2Me), 3.66 (3 H, s, OMe), 3.45 (1 H, s *gem*-diester CH), 3.35 (1 H, m, 5-H), 2.70 (1 H, d, *J* 7 Hz, 2-H), 2.19 (3 H, s, COMe), and 2.5—1.4 (6 H); *m/e* 450 (M^+) (Found: C, 50.35; H, 4.75. $C_{19}H_{22}FeO_9$ requires C, 50.7; H, 4.95%).

The diester complex (4) (0.20 g) gave, after purification on preparative layer chromatography, the tetraester (17) (0.18 g, 92%) as a yellow gum, which could not be crystallised but which appeared pure from its n.m.r. spectrum, $\nu_{max.}$ ($CHCl_3$) 2 060, 1 970, 1 755, and 1 735 cm^{-1}; δ 5.0 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 2 Hz, 3-H), 3.73 (6 H, s), 3.71 (3 H, s), and 3.69 (3 H, s) (4 × CO_2Me), 3.60 (3 H, s, OMe), 3.35 (3 H, m, 5-H, and 2 × *gem*-diester CH), 2.67 (1 H, d, *J* 7 Hz, 2-H), and 2.4—1.2 (8 H) (Found: M^+, 552. $C_{23}H_{28}FeO_{12}$ requires *M*, 552).

The β-keto-ester (11) (0.10 g) gave, after purification on preparative layer chromatography, the complex (19) (0.073 g, 75%), which could not be crystallised, $\nu_{max.}$ ($CHCl_3$) 2 060, 1 970, 1 755, and 1 730 cm^{-1}; δ 5.0 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 3 Hz, 3-H), 3.72 and 3.70 (9 H, 3 × CO_2Me), 3.61 (3 H, s, OMe), 3.54 (2 H, s, β-keto-ester CH_2), 3.47 (1 H, s, *gem*-diester CH), 3.4 (1 H, m, 5-H), 2.63 (1 H, d, *J* 7 Hz, 2-H), and 2.5—1.5 (6 H) (Found: M^+, 508. $C_{21}H_{24}FeO_{11}$ requires *M*, 508).

Removal of Iron from Complex (16).—The complex (0.68 g) was stirred with saturated ethanolic copper(II) chloride (20 ml) for 27 h at room temperature. The solution was poured into water (100 ml) and the product extracted in the usual way with ether, and purified by preparative layer chromatography on silica gel (20% ethyl acetate in benzene) to give the *cyclohexenone* (20) as an oil (0.367 g, 76%), $\nu_{max.}$ ($CHCl_3$) 1 755, 1 733, and 1 675 cm^{-1}; δ 7.05 (1 H, d, *J* 10 Hz, 3-H), 5.90 (1 H, d, *J* 10 Hz, 2-H) 3.72 (6 H, s) and 3.66 (3 H, s) (3 × CO_2Me) (*gem*-diester CH obscured at *ca.* 3.7), and 2.6—1.3 (12 H) (Found: M^+, 340.153 1. $C_{17}H_{24}O_7$ requires 340.152 1).

Tricarbonyl[4-(4-*methoxycyclohexa*-1,3-*dienyl*)*butyric acid*]-*iron* (22).—The ester (21) [2] (2.0 g) was hydrolysed as for (7), except that after work-up the product was extracted with ether in the usual way. Recrystallisation from hexane–dichloromethane gave (22) as a yellow crystalline *solid* (1.33 g, 69%), m.p. 86.5—88 °C, $\nu_{max.}$ (Nujol) 2 700—3 300, 2 050, 1 960, and 1 705 cm^{-1}; δ 11.6br (1 H, exchanges with D_2O, CO_2H), 5.20 (1 H, d, *J* 4 Hz, 2-H), 4.94 (1 H, d, *J* 4 Hz, 3-H), 3.48 (3 H, s, OMe), and 2.50—1.40 (10 H); *m/e* 336 (M^+) (Found: C, 50.1; H, 4.8. $C_{14}H_{16}Feo_6$ requires C, 50.05; H, 4.8%).

Tricarbonyl[5-(4-*methoxycyclohexa*-1,3-*dienyl*)*pentan*-2-

one]iron (23).—Reaction of the acid (22) (2.0 g) with methyllithium as for the preparation of (9) gave, after chromatography, the ketone as a yellow oil (1.5 g, 75%), $\nu_{max.}$ ($CHCl_3$) 2 045, 1 955, and 1 717 cm^{-1}; δ 5.18 (1 H, d, *J* 4 Hz, 2-H), 4.90 (1 H, d, *J* 4 Hz, 3-H), 3.43 (3 H, s, OMe), 2.14 (3 H, s, COMe), and 2.60—1.50 (10 H); *m/e* 334 (M^+), 2,4-dinitrophenylhydrazone, m.p. 120—122 °C.

Tricarbonyl[methyl 6-(4-methoxycyclohexa-1,3-dienyl)-3-oxohexanoatel]iron (24).—Treatment of the ketone (23) (1.16 g) with sodium hydride and dimethyl carbonate as for (10) gave the *keto-ester* (24) isolated from column chromatography as a yellow oil (1.14 g, 84%), $\nu_{max.}$ ($CHCl_3$) 2 050, 1 960, 1 750, and 1 720 cm^{-1}; δ 5.17 (1 H, d, *J* 4 Hz, 2-H), 4.92 (1 H, d, *J* 4 Hz, 3-H), 3.72 (3 H, s, CO_2Me), 3.44 (5 H, s, OMe, and keto-ester CH_2), and 2.7—1.6 (10 H), *m/e* 392 (M^+) (Found: C, 52.05; H, 5.2. $C_{17}H_{20}FeO_7$ requires C, 52.1; H, 5.15%).

Tricarbonyl[methyl 6-(4-methoxycyclohexa-2,4-dienylium)-3-oxohexanoate]iron Hexafluorophosphate (25).—Treatment of the keto-ester (24) (1.14 g) with triphenylmethylium tetrafluoroborate (2.5 g), followed by treatment with ammonium hexafluorophosphate, as for (11), gave the hexafluorophosphate (25) as a yellow gum after removal of solvent at 10^{-3} mmHg. A number of attempts to crystallize this material were unsuccessful, and it did not solidify even on prolonged storage at 0°, yield 0.95 g (61%), $\nu_{max.}$ (CH_3NO_2) 2 120, 2 075, 1 753, and 1 725 cm^{-1}; δ (CD_3CN) 6.82 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2.5 Hz, 3-H), 5.60 (1 H, d, *J* 6 Hz, 2-H), 3.95 (1 H, m, partly obscured, 5-H), 3.78 (3 H, s, CO_2Me), 3.65 (3 H, s, OMe), 3.46 (2 H, s, keto-ester CH_2), 3.0 (1 H, dd, J_{gem} 15, $J_{5,6}$ 6 Hz, *endo*-6-H), and 2.70—1.50 (7 H) (Found: C, 37.8; H, 3.3. $C_{17}H_{19}FeF_6O_7P$ requires C, 38.1; H, 3.55%).

Tricarbonyl[η-7–10-(methyl 9-methoxy-2-oxospiro[5.5]undeca-7,9-diene-1-carboxylate]iron (26) *and* (27).—A solution of (25) (0.72 g) in dichloromethane (20 ml) at −78 °C under nitrogen was stirred whilst triethylamine (0.14 g) in dichloromethane (5 ml) was added dropwise (syringe). Reaction appeared to be almost instantaneous (colour changes from orange to pale yellow) but the mixture was stirred at −78 °C for 20 min to ensure complete reaction, during which time a precipitate of triethylammonium hexafluorophosphate was thrown down. The mixture was poured into water and extracted in the usual way with ether. Removal of solvent gave the crude product as a pale yellow solid (0.47 g, 90%). Preparative layer chromatography (silica gel, 10% ethyl acetate in benzene) gave three bands. Extraction of the least polar band gave an oil (4–5 mg) the i.r. spectrum of which indicated the homologue of (13) (β-keto ester at 1 745 and 1 720, C=C absorption at 1 612 cm^{-1}). Extraction of the two more polar bands gave 0.20 and 0.22 g, respectively, of pale yellow crystalline material, both having m.p. 140—142°, and showing identical n.m.r. spectra, assignable to the readily equilibrated mixture (*ca.* 55 : 45) of diastereoisomers (26) and (27), $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, 1 750m, 1 730s, and 1 710s cm^{-1}; δ 5.15 (dd, $J_{1,2}$ 6, $J_{2,4}$ 2 Hz) and 5.00 (dd, $J_{1,2}$ 6, $J_{2,4}$ 2 Hz) (total 1 H 8-H of both), 3.83 and 3.80 (3.5 H total, 2 × s, CO_2Me of both and keto-ester CH of one, obscured), 3.72 (3 H, s, OMe), 3.4 (1 H, m, 10-H), 3.32 (0.5 H, s, remaining keto-ester CH), and 3.00—1.40 (9 H); *m/e* 390 (M^+) (Found: C, 52.1; H, 4.8. Calc. for $C_{17}H_{18}FeO_7$: C, 52.35; H, 4.65%).

Methyl 9-Methoxy-2-oxospiro[5.5]undeca-7,9-diene-1-carboxylate (28).—The complexes (26) and (27) (0.23 g) were stirred at 40° in benzene with freshly sublimed anhydrous trimethylamine *N*-oxide (1.0 g) for 2.5 h. The benzene solution was decanted, washed with brine, and dried ($MgSO_4$). Removal of solvent *in vacuo*, followed by passage through a short column of Florisil, gave the mixture of diastereoisomers (28) (0.07 g, 48%) as a pale yellow oil which contained *ca.* 5% aromatic impurity (n.m.r.), but was used without further purification for the next stage, $\nu_{max.}$ ($CHCl_3$) 1 750sh, 1 730, 1 712, 1 658, and 1 610 cm^{-1}; δ 5.9—5.5 (2 H, m, 7- and 8-H), 4.6 (1 H, m, 10-H), 3.76 (3 H, s, CO_2Me), 3.64 (3 H, s, OMe), 3.54 (0.5 H, s) and 3.35 (0.5 H, s) (keto-ester CH), and 3.00—1.40 (8 H); *m/e* 250 (M^+).

Methyl 2,9-Dioxospiro[5.5]undex-7-ene-1-carboxylate (29).—The crude dienol ether (28) (0.050 g) in methanol (3.0 ml) was stirred whilst a solution of oxalic acid (0.06 g) in water (0.6 ml) was added. After 0.5 h the mixture was poured into 0.5% aqueous sodium hydrogen carbonate and the product extracted with ether. Preparative layer chromatography (silica gel–ether) gave (29) as an oil which darkened on storage (0.025 g, 53%), $\nu_{max.}$ ($CHCl_3$) 1 745sh, 1 715, 1 675, 1 642, and 1 602 cm^{-1}; δ 6.87 (0.5 H, d, *J* 10 Hz) and 6.66 (0.5 H, d, *J* 10 Hz) (7-H of both isomers), 5.98 (0.5 H, d, *J* 10 Hz) and 5.85 (0.5 H, d, *J* 10 Hz) (8-H of both), 3.72 (s) and 3.71 (s) (3.5 H, CO_2Me of both, and keto-ester CH of one, obscured), 3.47 (0.5 H, s, keto-ester CH of one), and 2.70—1.50 (10 H) (Found: M^+, 236.105 6. $C_{13}H_{16}O_4$ requires *M*, 236.104 9).

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