

Organometallic Complexes in Synthesis. Part VI.¹ Some Oxidative Cyclisations of Tricarbonylcyclohexadieneiron Complexes

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Tricarbonylcyclohexadienyliron salts of type (2; $R^2 = +$), after reaction successively with a β -diketone or a β -keto-ester and manganese dioxide or lead dioxide, give tricarbonyl-*cis*-3a.7a-dihydrofuraniron complexes of type (3). Use of deuteriated intermediates indicated that the cyclisation occurs with specific loss of the 6-*endo*-proton.

THE reactions with nucleophiles of some carbonium salts derived from tricarbonylcyclohexadieneiron derivatives have been reported.^{2,3} Such processes are potentially useful in organic synthesis if the tricarbonyliron group can be removed in good yield. This question is discussed elsewhere,³ the usual reagents being iron(III) chloride or cerium(IV) salts.

We have reported² that manganese dioxide removes the tricarbonyliron group from its complex with 1-methoxycyclohexa-1,3-diene (1), but not from the complex with 2-methoxycyclohexa-1,3-diene (2; $R^2 = H$, $R^1 = OMe$), in experiments with a mixture of the two diene complexes. We have now separated these complexes chromatographically, and have confirmed the original observations, although (1) was oxidised to give anisole rather than 1-methoxycyclohexa-1,3-diene and (2; $R^1 = OMe$, $R^2 = H$) was relatively stable.

In order to investigate further the capabilities of the

reagent its action has been examined on compounds obtained by the reactions of some nucleophiles with the ion (2; $R^2 = +$). A new type of reaction occurred, involving oxidative cyclisation of enol forms to produce a new dihydrofuranoid ring, *e.g.* (3; $R^2 = Me$) from [2; $R^2 = CH(COMe)_2$] and (4) from (5) (for stereochemistry see later).

The structures were assigned on the bases of analyses and spectra. The analytical data and mass spectra of the oxidation products (3) and (4) indicated that each possessed two hydrogen atoms less than its precursor. This observation was confirmed by the ¹H n.m.r. spectra (Tables 1 and 2). The interpretation of the ¹H n.m.r. spectrum of (3; $R^1 = OMe$, $R^2 = Me$) was aided by spin-decoupling experiments. Irradiation at δ 5.17 (5-H) caused the doublet of doublets at δ 3.20 (4-H) to collapse to a doublet (J 4.5 Hz). Conversely, irradiation at δ 3.20 (4-H) caused the doublet of doublets at δ 5.17 (5-H) to collapse to a doublet (J 2 Hz). Irradiation at

¹ Part V, A. J. Birch and D. Williamson, preceding paper.

² A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

³ Part IV, A. J. Birch, K. B. Chamberlain, M. Haas, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882.

δ 5.02 (7a-H) caused the doublet of doublets at δ 3.42 (7-H) to collapse to a doublet (J 2 Hz) and the doublet of doublets at δ 3.60 (3a-H) to collapse to a doublet (J 4.5 Hz). Irradiation at δ 3.42 (7-H) caused the doublet of doublets at δ 5.02 (7a-H) to collapse to a doublet

absorptions at 1690 ($\alpha\beta$ -unsaturated ester) and 1640 cm^{-1} (enol ether), whereas compounds (3; $R^1 = \text{H}$, $R^2 = \text{Me}$) and (3; $R^1 = \text{OMe}$, $R^2 = \text{Me}$) showed strong absorption at 1650 cm^{-1} ($\alpha\beta$ -unsaturated ketone and enol ether).

In a polar solvent such as ethanol the u.v. absorption

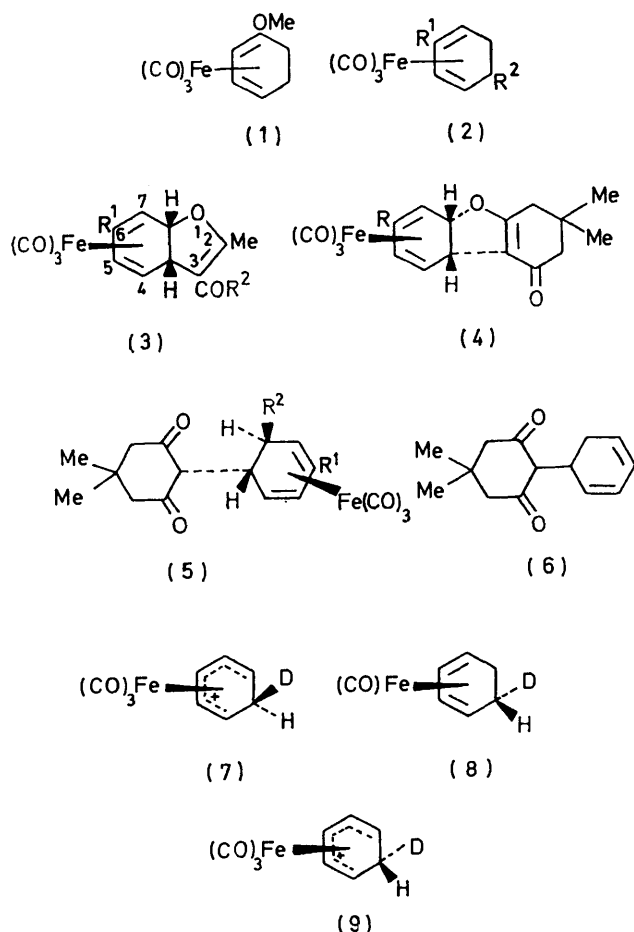
TABLE 1
 ^1H N.m.r. absorptions (δ values; J in Hz)

Compound (2)		1-H	R ¹	3-H	4-H	5-H	6-H	5-CH	Me
H	CH(COMe) ₂	3.28m	5.30m	5.30m	2.96m	2.96m	2.1m, 1.14dt, J 15, 3	3.28d, J 10	2.16s, 2.05s
OMe	CH(COMe) ₂	3.30m	3.62s	5.0dd, J 6, 3	2.28dd, J 6, 3	2.73tt, J 10, 3	2.04m, 1.22dt, J 15, 3	3.30d, J 10	2.18s, 2.06s

TABLE 2
 ^1H N.m.r. absorptions (δ values; J in Hz)

Compound (3)		3a-H	4-H	5-H	R ¹	7-H	7a-H	Me
H	Me	3.48m	3.10dd, J 4, 3	5.44m	5.44m	3.48m	4.98dd, J 8, 4	2.20s, 2.09s
OMe	Me	3.60dd, J 9, 4.5	3.20dd, J 3.5, 4.5	5.17dd, J 3.5, 2	3.68s	3.42dd, J 4, 2	5.02dd, J 9, 4	2.22s, 2.10s

(J 9 Hz) and the doublet of doublets at δ 5.17 (5-H) to collapse to a doublet (J 3.5 Hz).



The i.r.-spectra of compounds (3; $R^1 = \text{H}$, $R^2 = \text{OEt}$) and (3; $R^1 = \text{OMe}$, $R^2 = \text{OEt}$) showed strong

of (3) is at a much longer wavelength (280 nm) than that (*ca.* 265 nm) to be expected of the chromophore, but in the less polar hexane this absorption is at 265 nm. This is probably explicable in terms of polarisation of the new C-O bond, which is incipiently ionised in the more polar solvent. When the diketone (5; $R^1 = R^2 = \text{H}$) and lead dioxide were heated under reflux in benzene the cyclic ether (4; $R = \text{H}$) was produced in 75% yield. The action of iron(III) chloride in *n*-hydrochloric acid on the complex (5; $R^1 = R^2 = \text{H}$) generated (6) in good yield. The complexes [2; $R^1 = \text{H}$ or OMe, $R^2 = \text{CH}(\text{CO}_2\text{Et})_2$] were not oxidised by manganese dioxide.

In order to gain more information about the mechanism of the ring closure the reaction was repeated on various deuteriated intermediates. Tricyclopentadienyliron hexafluorophosphate (7) was prepared by treating tricyclopentadienyliron fluoro-borate with sodium borodeuteride gave tricyclopentadienyliron-6-*exo*-deuteriocyclohexa-1,3-dieneiron (8), which on treatment with triphenylmethyl fluoroborate regenerated the salt with 50% deuterium in the 6-*exo*-position (9). Treatment of this salt with dimedone and cyclisation with manganese dioxide gave the cyclisation product with no loss of deuterium. It appears, therefore, that the cyclisation occurs with specific loss of the 6-*endo*-proton. Oxidation may therefore proceed through the iron atom with transfer of *endo*-hydride, or at any rate

⁴ A. J. Birch and M. A. Haas, *J. Chem. Soc. (C)*, 1971, 2465.

of the *endo* C-H electrons to the oxidising agent *via* the iron. The monoketone complexes³ are not oxidised similarly nor are the unsubstituted or 2-methoxycyclohexa-1,3-dieneiron complexes affected. The process may well be a concerted attack by the OH of the enol, assisting loss of electrons from the *endo* C-H bond broken.

Subsequent to this work an X-ray crystallography structure⁵ of compound (3; R¹ = OMe, R² = Me) denoted the stereochemistry shown. This is important in demonstrating both the *cis* ring junction and the *exo*-attack of the nucleophile, which is presumably general for this class of reaction (see also ref. 2).

A further discussion of the formation of compound (7) and some related reactions will be published elsewhere.⁶

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were measured for chloroform solutions with a JASCO IRA-1 spectrometer. U.v. spectra were measured with a Unicam SP 800 spectrometer. ¹H N.m.r. spectra were determined for solutions in deuteriochloroform with a Varian HA-100 spectrometer (tetramethylsilane as internal standard), and mass spectra were measured with an A.E.I. MS-902 spectrometer. The activated manganese dioxide was supplied by Winthrop Laboratories and the silica used for chromatography was Merck 70—325 mesh. The lead dioxide was supplied by May and Baker.

5-(1-Acetylacetylonyl)cyclohexa-1,3-dienetricarbonyliron [2; R¹ = H, R² = CH(COMe)₂] and tricarbonyl-5-(4,4-dimethyl-2,5-dioxocyclohexyl)cyclohexa-1,3-dieneiron (5; R¹ = R² = H) were prepared as previously described.²

Tricarbonyl-5-(1-ethoxycarbonylacetylonyl)cyclohexa-1,3-dieneiron [2; R¹ = H, R² = CH(COMe)(CO₂Et)].—A solution of tricarbonylcyclohexadienyliron fluoroborate (2; R¹ = H, R² = +) (0.3 g) and ethyl acetoacetate (1 ml) in aqueous ethanol was heated under reflux for 2 h. After addition of water, extraction with ether gave an orange oil which was chromatographed on silica to give the *β*-keto-ester [2; R¹ = H, R² = CH(COMe)(CO₂Et)] as a yellow oil (0.24 g) (Found: C, 51.5; H, 4.9%; M⁺, 348. C₁₅H₁₆FeO₆ requires C, 51.7; H, 4.7%; M, 348); ν_{max} 2040, 1960, 1740, and 1717 cm⁻¹; λ_{max} (EtOH) 225 nm.

5-(1-Acetylacetylonyl)-2-methoxycyclohexa-1,3-dienetricarbonyliron [2; R¹ = OMe, R² = CH(COMe)₂].—This was prepared from tricarbonyl-2-methoxycyclohexadienyliron fluoroborate (0.5 g) and acetylacetone (2 ml) by a method similar to that just described to give the *β*-diketone [2; R¹ = OMe, R² = CH(COMe)₂] (0.42 g) as pale yellow prisms, m.p. 84—86° (from chloroform-hexane) (Found: C, 51.7; H, 4.75%; M⁺, 348. C₁₆H₁₈FeO₆ requires C, 51.7; H, 4.7%; M, 348); ν_{max} 2050, 1960, 1720, and 1705 cm⁻¹; λ_{max} (EtOH) 240 and 260 nm.

Tricarbonyl-5-(4,4-dimethyl-2,5-dioxocyclohexyl)-2-methoxycyclohexa-1,3-dieneiron (5; R¹ = OMe, R² = H).—This was prepared similarly from the salt (2; R¹ = OMe, R² = +) (0.6 g) and dimedone (0.3 g) to give plates of the *β*-diketone (5; R¹ = OMe, R² = H) (0.73 g), m.p. 135° (decomp.) (from aqueous ethanol) (Found: C, 56.0; H, 5.4%; M⁺, 388. C₁₈H₂₀FeO₆ requires C, 55.8; H, 5.2%; M, 388).

Tricarbonyl-5-(1-ethoxycarbonylacetylonyl)-2-methoxycyclohexa-1,3-dieneiron [2; R¹ = OMe, R² = CH(COMe)-

(CO₂Et)].—This was prepared similarly from the salt (2; R¹ = OMe, R² = +) (1.0 g) and ethylacetoacetate (2 ml) to give the *β*-keto-ester [2; R¹ = OMe, R² = CH(COMe)(CO₂Et)] as a yellow oil (0.8 g) (Found: C, 50.6; H, 4.6%; M⁺, 378. C₁₆H₁₈FeO₇ requires C, 50.8; H, 4.75%; M, 378); ν_{max} 2050, 1960, 1740, and 1720 cm⁻¹; λ_{max} (EtOH) 238 nm.

Reaction of the Foregoing Complexes with Activated Manganese Dioxide.—The following general procedure was used in all cases. The complex (0.2 g) and activated manganese dioxide (1.0 g) were heated under reflux in benzene for 2 h. The cooled solution was filtered and the manganese dioxide washed well with benzene. The filtrate and combined washings were evaporated and the product was filtered through a short silica column.

5-(1-Acetylacetylonyl)cyclohexa-1,3-dienetricarbonyliron [2; R¹ = H, R² = CH(COMe)₂] gave tricarbonyl-2-methyl-3-acetyl-3a,7a-dihydrobenzofuraniron (3; R¹ = H, R² = Me) as prisms (85%), m.p. 113—116° (from chloroform) (Found: C, 53.15; H, 4.1%; M⁺, 316. C₁₄H₁₂FeO₅ requires C, 53.16; H, 3.9%; M, 316); λ_{max} (EtOH) 215 and 279 (ε 14,000) nm, λ_{max} (hexane) 217 and 264sh nm.

Tricarbonyl-5-(4,4-dimethyl-2,5-dioxocyclohexyl)cyclohexa-1,3-dieneiron (5; R¹ = R² = H) gave tricarbonyl-3,4,5a,9a-tetrahydro-3,3-dimethyldibenzofuran-1(2H)-oneiron (4; R = H) as pale yellow plates (86%), m.p. 169—172° (from chloroform) (Found: C, 56.9; H, 4.8%; M⁺, 356. C₁₇H₁₆FeO₆ requires C, 57.2; H, 4.6%; M, 356); ν_{max} 2050, 1960, 1660, and 1620 cm⁻¹; λ_{max} (EtOH) 213 and 276 nm, λ_{max} (hexane) 218 and 264sh nm; δ 5.46 (2H, m, 7-, 8-H), 5.14 (1H, dd, J 10 and 4 Hz, 5a-H), 3.64 (2H, m, 6-, 9a-H), 3.10 (1H, dd, J 4 and 3 Hz, 9-H), 2.13 (4H, s, 2-, 4-H), 2.06 (3H, s, Me), and 2.04 (3H, s, Me).

Tricarbonyl-5-(1-ethoxycarbonylacetylonyl)cyclohexa-1,3-dieneiron [2; R¹ = H, R² = CH(COMe)(CO₂Et)] gave tricarbonyl(ethyl 3a,7a-dihydro-2-methylbenzofuran-3-carboxylate)iron (3; R¹ = H, R² = OEt) (55%) as pale yellow plates, m.p. 92—94° (chloroform-hexane) (Found: C, 51.9; H, 4.2%; M⁺, 346. C₁₅H₁₄FeO₆ requires C, 52.1; H, 4.2%; M, 346); λ_{max} (EtOH) 222 and 265sh nm; δ 5.46 (2H, m, 5-, 6-H), 5.0 (1H, dd, J 8 and 4 Hz, 7a-H), 4.16 (2H, q, J 6 Hz, CO₂CH₂Me), 3.66 (2H, m, 7-, 3a-H), 3.10 (1H, dd, J 4 and 3 Hz, 4-H), 2.06 (3H, s, Me), and 1.30 (3H, t, J 6 Hz, Me).

5-(1-Acetylacetylonyl)-2-methoxycyclohexa-1,3-dienetricarbonyliron [2; R¹ = OMe, R² = CH(COMe)₂] gave 3-acetyl-3a,7a-dihydro-6-methoxy-2-methylbenzofurantricarbonyliron (3; R¹ = OMe, R² = Me) (96%) as pale yellow prisms, m.p. 104—106° (from hexane) (Found: C, 52.2; H, 4.5%; M⁺, 346. C₁₅H₁₄FeO₆ requires C, 52.1; H, 4.2%; M, 346); λ_{max} (EtOH) 215 and 279 (ε 10,600) nm, λ_{max} (hexane) 230 and 270sh nm.

Tricarbonyl-5-(4,4-dimethyl-2,5-dioxocyclohexyl)-2-methoxycyclohexa-1,3-dieneiron (5; R¹ = OMe, R² = H) gave tricarbonyl-3,4,5a,9a-tetrahydro-3,3-dimethyldibenzofuran-1(2H)-oneiron (4; R = OMe) (75%) as pale yellow plates, m.p. 116—119° (from chloroform-hexane) (Found: C, 56.2; H, 5.1%; M⁺, 386. C₁₈H₁₈FeO₆ requires C, 56.1; H, 4.9%; M, 386); ν_{max} 2050, 1960, 1655, and 1614 cm⁻¹; λ_{max} (EtOH) 240 and 275 nm; δ 5.20 (2H, m, 5a-, 8-H), 3.70 (3H, s, OMe), 3.60 (1H, m, 9a-H), 3.45 (1H, dd, J 4 and 2 Hz, 6-H), 3.25 (1H, dd, J 5 and 4 Hz, 9-H), 2.16 (4H, s, 2-, 4-H), and 1.05 (6H, s, 2Me).

⁵ B. Anderson, personal communication.

⁶ A. J. Birch and D. J. Thompson, to be published.

Tricarbonyl-5-(1-ethoxycarbonylacetyl)-2-methoxycyclohexa-1,3-dieneiron [2; $R^1 = \text{OMe}$, $R^2 = \text{CH}(\text{COMe})(\text{CO}_2\text{Et})$] gave *tricarbonyl(ethyl 3a,7a-dihydro-6-methoxy-2-methylbenzofuran-3-carboxylate)iron* (3; $R^1 = \text{OMe}$, $R^2 = \text{OEt}$) (50%) as pale yellow prisms, m.p. 75–77° (from hexane) (Found: C, 50.8; H, 4.5%; M^+ , 376. $\text{C}_{16}\text{H}_{16}\text{FeO}_7$ requires C, 51.0; H, 4.3%; M , 376); λ_{max} (EtOH) 230 and 265sh nm; δ 5.19 (1H, dd, J 4 and 2 Hz, 5-H), 5.02 (1H, dd, J 10 and 4 Hz, 7a-H), 5.84 (2H, q, J 7 Hz, $\text{CO}_2\text{-CH}_2\text{Me}$), 3.68 (3H, s, OMe), 3.56 (1H, dd, J 10 and 3 Hz, 3a-H), 3.42 (1H, dd, J 4 and 2 Hz, 7-H), 3.16 (1H, dd, J 4 and 3 Hz, 4-H), 2.06 (3H, s, Me), and 2.30 (3H, t, J 7 Hz, Me).

Oxidation of the Diketone (5; $R^1 = R^2 = \text{H}$) with *Lead Dioxide*.—The diketone (0.2 g) and lead dioxide (1.0 g) were heated under reflux in benzene for 2 h. The cooled solution was filtered through Celite; removal of the solvent gave a crystalline solid which was recrystallised from chloroform to give pale yellow plates of tricarbonyl-3,4,5a,9a-tetrahydro-3,3-dimethyldibenzofuran-1(2H)-oneiron (4; $R = \text{H}$), m.p. 168–171°.

Oxidation of the Complexes with Iron(III) Chloride.—Reaction of the complex (5; $R^1 = R^2 = \text{H}$) (0.1 g) with iron(III) chloride (1.0 g) in acidified ethanol at room temperature for 5 min gave after dilution with water and ether extractions, 4,2-cyclohexa-2,4-dienyl-5,5-dimethylcyclohexane-1,3-dione (6) (85%).

When the complex (4; $R = \text{H}$) was treated with the same reagent no reaction occurred, even during 24 h.

Reaction of the cyclic ether (4) with either iron(III) chloride in acetonitrile or cerium(IV) ammonium nitrate in acetonitrile removed of the tricarbonyliron group but gave complex mixtures from which no pure compounds were isolated.

Reaction of Tricarbonyl-1-methoxycyclohexa-1,3-dieneiron (1) with Manganese Dioxide.—The mixture of tricarbonyl-1-methoxycyclohexa-1,3-dieneiron (1) and the 2-methoxy-isomer (2; $R^1 = \text{OMe}$, $R^2 = \text{H}$) obtained by reaction of 1-methoxycyclohexa-1,4-diene with iron pentacarbonyl was separated by chromatography on a silica column (pentane as developing solvent). The 1-methoxy-isomer (1) on treatment with manganese dioxide as already described was rapidly oxidised to anisole. The 2-methoxy-isomer (2; $R^1 = \text{OMe}$, $R^2 = \text{H}$) was oxidised slowly to the same product.

Tricarbonyl-6-endo-deuteriocyclohexadienyliron Hexafluorophosphate (7).—A solution of tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (2; $R^1 = \text{OMe}$, $R^2 = \text{H}$) (1.0 g) in deuteriosulphuric acid (1.5 ml) was kept at room temperature for 15 min, then carefully saturated with ether, causing the salt to precipitate. Repeated trituration with ether removed any neutral complexes and the precipitated salt was dissolved in a small volume of water. Addition of a 10% solution of ammonium hexafluorophosphate precipitated the salt (7) (95%); δ ($\text{CF}_3\text{-CO}_2\text{H}$) 7.26 (1H, t, 3-H), 5.85 (2H, t, 2-, 4-H), 4.3 (2H, d, 1-, 5-H), and 2.08br (1H, s, *exo*-6-H).

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