

Dichlorocarbene Addition to Tricarbonyliron Complexes of Polyenes

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Dichlorocarbene adds to the unco-ordinated double bonds in the tricarbonyliron complexes of cycloheptatriene and myrcene to give (2) and (5) respectively. Copper(II) oxidation of (5) liberates the ligand (6). The tricarbonyliron complexes of ergosteryl acetate (11) and cyclo-octatetraene (12) fail to react with dichlorocarbene. The possibility of aromatic character in the organic ligand in (12) is discussed.

THE modification of the reactivity of polyenes by complex formation with transition metals is a subject of wide synthetic interest. This paper describes the results of a study of the reaction of dichlorocarbene with the tricarbonyliron complexes of a selection of polyenes.

Cycloheptatrienetricarbonyliron (1) reacted with dichlorocarbene, produced by the reaction of chloroform with a suspension of potassium *t*-butoxide in heptane, to give a moderate yield of a product, $C_{11}H_8Cl_2FeO_3$. Comparison of the n.m.r. spectrum of this compound with that of (1) showed that two one-proton absorptions in the region δ 4–5 in the spectrum of (1) were absent from that of the product which contained multiplets in the region δ 1–2, due to two protons, overlapping with absorption attributable to the methylene group of the cycloheptatriene residue. There was no significant change in the carbonyl absorptions in the i.r. spectrum, and it appeared that the dichlorocarbene had added to the uncomplexed double bond of (1) to give compound (2). This conclusion was confirmed by the synthesis of (2) by reaction of 8,8-dichlorobicyclo[5.1.0]octa-2,4-diene (3) with enneacarbonyldi-iron or (benzylideneacetone)tricarbonyliron.¹

(Myrcene)tricarbonyliron (4) likewise reacted with dichlorocarbene to give a compound, $C_{14}H_{16}Cl_2FeO_3$, identified as (5). Comparison of the n.m.r. spectra of (4) and the product showed that the major changes were the upfield shift of the two methyl singlets of (4) by *ca.* 0.5 p.p.m. and the change of a two-proton multiplet at δ *ca.* 5 in the spectrum of (4) into a slightly broadened one-proton triplet, δ 5.08, in the spectrum of the product, both of which are fully consistent with the formation of (5). The two one-proton signals at δ *ca.* 0 in the n.m.r. spectrum of (4), attributed to the 'internal' protons of the terminal methylene groups of the co-ordinated butadiene system, are unchanged in chemical shift and coupling in the n.m.r. spectrum of the product, showing that dichlorocarbene addition has not affected the metal complexed diene system. In the spectrum of the product, one of these protons absorbing at high field seems to be coupled to the proton responsible for the triplet at δ 5.08, which is assigned to the proton at position 2 of the complexed butadiene system.

The independent synthesis of (5) *via* prior formation of (6) was not feasible as dichlorocarbene was expected² to add preferentially to the conjugated double bonds in myrcene. G.l.c. analysis showed that the reaction of dichlorocarbene with myrcene gave a complex mixture of products which was not further investigated. Since it appeared that formation of the tricarbonyliron complex

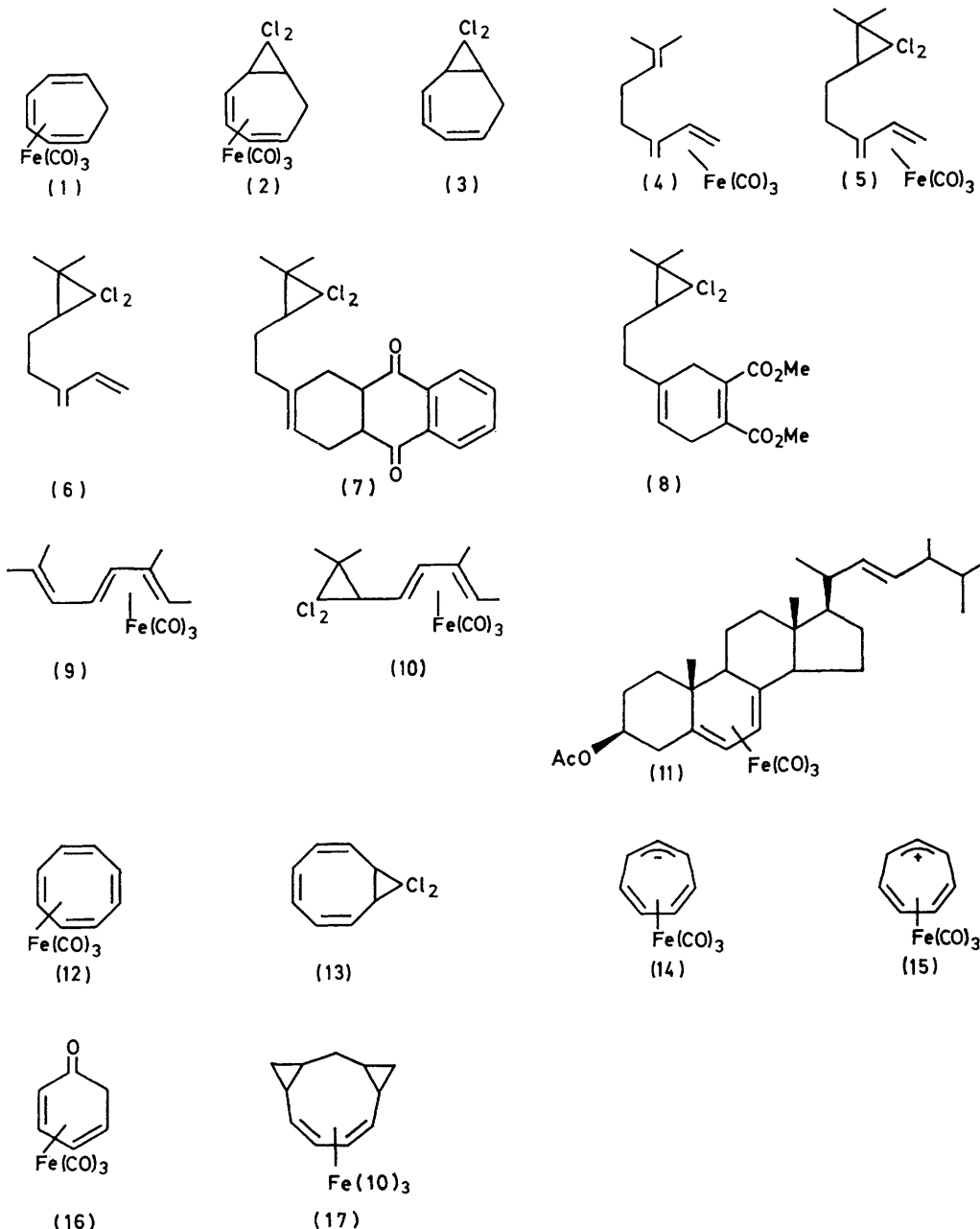
protected the conjugated diene from attack, as in the case of (1), an attempt was made to realise the synthetic potential of this type of protecting group by liberation of the ligand (6). An attempt to oxidise (5) with trimethylamine *N*-oxide³ was unsuccessful, but oxidation with copper(II) chloride⁴ gave (6) as an oil which was characterised by its ¹H and ¹³C n.m.r. spectra and also by conversion into the Diels–Alder adducts with naphthoquinone (7) and dimethyl butynedioate (8). An attempt to isolate the adduct of dibromocarbene with (4) was unsuccessful. A crude oily product was obtained which decomposed violently during vacuum distillation.

An attempt was made to perform a similar sequence of reactions on the tricarbonyliron complex of *allo*-ocimene (1,7-dimethylocta-2,4,6-triene) (9). The reaction of dichlorocarbene with (9) gave a product which could be isolated in a crude form as an oil, but this could not be purified and decomposed quite vigorously at 100° during an attempted vacuum distillation. It seems at first sight a little surprising that this compound, which is assumed to be (10) should be so much less stable than (2) which was successfully distilled under reduced pressure. It may be that the greater conformational flexibility of (10) is responsible for the reduced stability. An attempt to obtain the free ligand by oxidation of the crude reaction product with copper(II) chloride was unsuccessful. G.l.c. analysis of the oily product showed it to contain a large number of components with no one predominating.

Two polyene tricarbonyliron complexes failed to react with dichlorocarbene. (Ergosteryl acetate)tricarbonyliron (11) was recovered unchanged after treatment with potassium *t*-butoxide and chloroform. This failure to react may be ascribed to steric hindrance of the uncomplexed double bond, although this was unexpected.⁵ A much more surprising failure was that of cyclo-octatetraenetricarbonyliron (12), which was recovered unchanged after treatment with potassium *t*-butoxide and chloroform, sodium trichloroacetate in boiling dimethoxyethane,⁶ and bromodichloromethylphenylmercury in boiling benzene.⁷ There can be no question here of steric hindrance as the polyene ligand is not expected to be significantly less accessible than in (1),⁸ and cyclo-octatetraene itself readily undergoes a typical addition reaction with dichlorocarbene to give (13).⁹ An electronic explanation is tentatively proposed. Organic chemists are well aware that aromatic character in cyclic conjugated polyenes reduces the reactivity of the π -electron system very markedly. If co-ordination

of a tricarbonyliron group onto a polyene were effectively to add or subtract two electrons from the polyene π -system then a cyclic conjugated polyene with $4n$ π -electrons would, when complexed, have an effective π -electron population conforming to the Huckel ($4n + 2$) rule. The resistance of complex (12) to catalytic

$\text{Fe}(\text{CO})_3$ may have unexpected stability. It has been reported¹³ that (1) is deprotonated by butyl-lithium in tetrahydrofuran to give a dark red anion (14). During the course of the work with (1) it was observed that (1) dissolved in potassium t-butoxide in t-butyl alcohol to give an intensely red solution. Since t-butyl alcohol has



hydrogenation, bromine addition,¹⁰ and normal Diels-Alder reactions¹¹ is also consistent with this suggestion, as is the marked downfield shift of the n.m.r. absorptions (δ 6.1 and 6.4)^{8b} due to the protons on the uncomplexed part of the cyclic ligand in (12) compared with the absorption of free cyclo-octatetraene (δ 5.7).¹²

Another accidental observation during this work also suggests that a monocyclic 8π electron ligand attached to

a pK_a of 19.2¹⁴ this suggests that the pK_a of (1) must be in the region of 20 in contrast to the pK_a 36 for uncomplexed cycloheptatriene,¹⁵ whose anion is anti-aromatic. Also consistent with the proposal are the observations that the tricarbonyliron complex of tropylium cation (15) is slightly less stable than free tropylium cation,¹⁶ and that the trityl cation adds to (1) rather than abstract a hydride ion to form (15).¹⁷ If the $\text{Fe}(\text{CO})_3$

group effectively adds or subtracts two electrons from the ligand π -system then the tricarbonyliron complexed tropylium ion would be antiaromatic as would be the unknown tricarbonyliron complex of benzene. The failure of the cyclohexadienone complex (16) to enolise¹⁸ might also be explained in this way.

In contrast to the failure of (12) to react with dichlorocarbene, Reger has reported¹⁹ that (12) undergoes reaction with iodomethylzinc iodide to give (17). In view of the substantial structural change and the uncertainty of the mechanism, it is doubtful whether this result can be usefully compared with those reported here.

EXPERIMENTAL

¹H N.m.r. spectra were measured with a Varian HA 100 spectrometer. ¹³C N.m.r. spectra were measured with a JEOL PFT-100 spectrometer. I.r. spectra were measured on Perkin-Elmer PE 180, 457, and 257 spectrometers.

2—5- η -(8,8-Dichlorobicyclo[5.1.0]octa-2,4-diene)tricarbonyliron (2).—(A) Cycloheptatrienetricarbonyliron^{17,20} (22 ml, 30 g) in heptane (200 ml) was added to a suspension of potassium t-butoxide (from 16 g potassium) in heptane²¹ (ca. 100 ml) and the mixture was cooled in ice. A mixture of chloroform (60 ml; dried over concentrated sulphuric acid and redistilled) and hexane (100 ml) was added dropwise with stirring over 0.5 h. After stirring at room temperature for 1 h, dilute hydrochloric acid (250 ml, 2M) was added and the organic layer was separated, washed with water, and dried (MgSO₄). Evaporation of the solvent left a dark brown oil (35.5 g). A sample was distilled giving the *adduct* (2) as an orange oil (38%), b.p. 90–100° at 0.2 mmHg, solidifying to yellow crystals, m.p. 66° (from methanol) (Found: C, 41.8; H, 2.5. C₁₁H₈Cl₂FeO₃ requires C, 41.9; H, 2.5%), ν_{\max} (heptane) 2 050, 2 040(w), 1 983, 1 979, and 1 943(w) cm⁻¹, δ_{H} (CDCl₃) 1.5–2.0 (2 H, m), 2.0–2.5 (2 H, m), 2.8–3.1 (1 H, m), 3.22 (1 H, dt, *J* 8, 1 Hz), and 5.1–5.4 (2 H, m); *m/e* 314 (*M*⁺), calc. for C₁₁H₈⁵⁶Cl₂⁵⁶FeO₃: *M*, 314.

(B) Addition of cycloheptatrienetricarbonyliron in hexane to a solution of potassium t-butoxide in *t*-butyl alcohol gave a dark red solution. Addition of chloroform in hexane to this mixture at 0° gave a product identified as (2) by t.l.c. comparison.

(C) A mixture of 8,8-dichlorobicyclo[5.1.0]octa-2,4-diene (3)²² (3 ml), (benzylideneacetone)tricarbonyliron¹ (2 g), and hexane (75 ml) was boiled under reflux under nitrogen for 3.5 h. The product was separated chromatographically on silica gel from which was eluted [benzene–light petroleum (b.p. 40–60°) 1 : 4] as a pale yellow band. Evaporation of the solvent left an oil containing unchanged compound (3), which was distilled off at 70° and 0.05 mmHg. The residual yellow oil (2.1 g, 95%) was identified as (2) by comparison of i.r. spectra of liquid films.

(D) The reaction of (3) (0.25 g) with enneacarbonyldiiron (0.5 g) in boiling ether (10 ml) for 3 h gave (2), identified by t.l.c. analysis of the crude mixture.

1,1-Dichloro-2,2-dimethyl-3-[(3a,3,4,5- η -tricarbonylferrio)-3-methylenepent-4-enyl]cyclopropane (5).—The reaction of (myrcene)tricarbonyliron²³ (4) in heptane with potassium t-butoxide and chloroform, following the procedure described above, gave a crude oil which was separated chromatographically [silica gel; light petroleum (b.p. 40–60°)] into unchanged starting material and a slower moving component. Distillation of the latter gave the *adduct* (5)

as an orange oil (55%), b.p. 108–112° at 0.05 mmHg (Found: C, 47.6; H, 4.7; Cl, 20.1. C₁₄H₁₆Cl₂FeO₃ requires C, 46.8; H, 4.5; Cl, 19.8%), δ_{H} (CCl₄) –0.04 (1 H, dd, *J* 8, 2 Hz), 0.15 (1 H, d, *J* 2 Hz), 0.8–1.4 (1 H, m), 1.04 (3 H, s), 1.24 (3 H, s), 1.4–2.0 (4 H, m), 2.0–2.6 (2 H, m), and 5.08 (1 H, t, *J* 8 Hz), ν_{\max} (heptane) 2 053, 1 988, and 1 977 cm⁻¹.

1,1-Dichloro-2,2-dimethyl-3-(3-methylenepent-4-enyl)-cyclopropane (6).—Potassium (10 g) was dissolved in dry *t*-butyl alcohol (250 ml) under nitrogen and ca. 50 ml of the excess of alcohol was distilled off. Heptane (50 ml) was added and the mixture was cooled to 0° to give a mobile slurry. (Myrcene)tricarbonyliron (4) (12 ml, 14.2 g) was added followed by dropwise addition of chloroform (30 ml) with stirring. The mixture was stirred at 0° for 1 h, then evaporated under reduced pressure. The residue was extracted with cold methanol (200 ml) and copper(II) chloride (20 g CuCl₂·2H₂O) was added to the methanolic solution. After stirring for several hours gas evolution ceased and the mixture was filtered and the residue washed well with methanol. Evaporation of the methanolic solution left an oil which was dissolved in ether and the ethereal solution was washed with dilute hydrochloric acid, sodium hydrogencarbonate solution, and water and then dried (CaCl₂). Evaporation of the ether left a brown oil (10.1 g) which on distillation gave the *cyclopropane* (6) as a slightly yellow oil (4 g, 45%), b.p. 84–88° at 2 mmHg, 46° at 0.1 mmHg. A sample was purified for analysis by g.l.c. (Found: C, 60.0; H, 7.5. C₁₁H₁₆Cl₂ requires C, 60.2; H, 7.3%), δ_{H} (CCl₄) 0.8–1.2 (1 H, m), 1.12 (3 H, s), 1.30 (3 H, s), 1.4–1.8 (2 H, m), 2.2–2.5 (2 H, m), 4.98 (2 H, s), 5.00 (1 H, d, *J* 11 Hz), 5.19 (1 H, d, *J* 18 Hz), and 6.25 (1 H, dd, *J* 18, 11 Hz), δ_{C} (CDCl₃) 17.2 (q), 24.8 (t + q), 29.5 (s), 30.3 (t), 38.3 (d), 71.9 (s), 113.5 (t), 116.4 (t), 138.4 (d), and 145.4 (s).

2-[2-(2,2-Dichloro-3,3-dimethylcyclopropyl)ethyl]-1,4,4a,10a-tetrahydro-9,10-anthraquinone (7).—A mixture of the diene (6) (0.9 g), 1,4-naphthoquinone (0.7 g), and benzene (3 ml) was boiled under reflux under nitrogen for 1 h. Evaporation of the solvent left an oil from which preparative t.l.c. (silica gel and benzene) separated the *Diels–Alder adduct* (7) as lemon-yellow plates (0.8 g, 51%), m.p. 133–134° (from ethanol) (Found: C, 67.1; H, 5.8; Cl, 19.0. C₂₁H₂₂Cl₂O₂ requires C, 66.8; H, 5.8; Cl, 18.8%), ν_{\max} (KBr) 1 661 cm⁻¹.

1,2-Bismethoxycarbonyl-4-[2-(2,2-dichloro-3,3-dimethylcyclopropyl)ethyl]cyclohexa-1,4-diene (8).—A mixture of the diene (6) (1 g), dimethyl butynedioate (0.6 ml), and benzene (2 ml) was boiled under reflux for 2 h. Evaporation of the solvent left a thick oil from which medium pressure liquid chromatography separated the *adduct* (8) as an oil, b.p. 190° at 0.04 mmHg (Found: C, 56.5; H, 6.1. C₁₇H₂₂Cl₂O₄ requires C, 56.5; H, 6.1%), ν_{\max} (film) 1 729 cm⁻¹, δ_{H} (CDCl₃) 1.0–1.2 (1 H, m), 1.14 (3 H, s), 1.32 (3 H, s), 1.5–1.7 (2 H, m), 2.0–2.2 (2 H, m), 2.8–3.1 (4 H, m), 3.76 (6 H, s), and 5.48 (1 H, s).

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Note added in proof. With reference to the discussion of compound (12) on p. 1717, a recent paper (J. Aihara, *Bull. Chem. Soc. Japan*, 1978, **51**, 1541) reports molecular-orbital calculations which predict aromatic stabilization in (12) and other tricarbonyl complexes.