

125. *Metal Derivatives of Conjugated Dienes. Part I.*
Butadiene- and cycloHexadiene-iron Tricarbonyls.

By B. F. HALLAM and P. L. PAUSON.

cycloHexa-1:3-diene reacts with iron carbonyl in the same manner as butadiene.¹ The properties of the resultant diene-iron tricarbonyls have been studied and their structures are discussed.

THE formation of butadieneiron tricarbonyl, $C_4H_6Fe(CO)_3$, from butadiene and iron pentacarbonyl was first reported by Rheilen, Gruhl, Hessling, and Pfrengle¹ in 1930 and later formed the subject of a patent by Veltman.² However, the efforts of the former authors to extend the reaction to other dienes led only to ill-defined products of the approximate composition $(C_5H_8)_2Fe(CO)_3$ and $(C_5H_8)_3Fe(CO)_3$ from isoprene and $(C_6H_{10})_2Fe(CO)_3$ from dimethylbutadiene and no further work on this interesting group of compounds has appeared. The present reinvestigation, stimulated by our interest in the reaction of iron carbonyls with *cyclopentadiene*,^{3,4} was initiated to obtain evidence on the structure of butadieneiron tricarbonyl.

Rheilen *et al.*¹ tentatively considered structure (I) for this compound. However, it appears extremely unlikely that even a "chelated" dialkyl of iron could be so remarkably stable as this substance. Its thermal stability is evident from its formation at 100–150° and from the fact that repeated distillation leaves it unchanged. We have kept a sample in a refrigerator for more than a year. The compound can be recovered unchanged from its solutions in pyridine, glacial acetic acid, and even concentrated sulphuric acid. It is likewise unaffected by hydrogen in the presence of Adams catalyst and by boiling with maleic anhydride in benzene solution for 48 hr.

Although a number of alkyl derivatives of iron^{4,5} and other transition-metal carbonyls^{6,7} have been described, the metal atom in all these may be regarded as attaining

¹ Rheilen, Gruhl, Hessling, and Pfrengle, *Annalen*, 1930, **482**, 161.

² Veltman, U.S.P. 2,409,167; *Chem. Abs.*, 1947, **41**, 595.

³ Hallam, Mills, and Pauson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 313.

⁴ Hallam and Pauson, *J.*, 1956, 3030.

⁵ Piper and Wilkinson, *Chem. and Ind.*, 1955, 1296; *Naturwiss.*, 1956, **43**, 15; *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

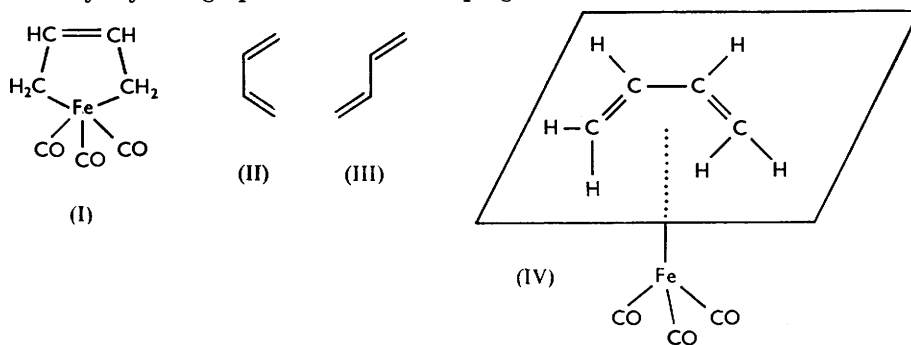
⁶ Fischer, Hafner, and Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.

⁷ Closson, Kozikowski, and Coffield, *J. Org. Chem.*, 1957, **22**, 598.

the electronic configuration of the next inert gas. Thus, by analogy to the alkylmanganese pentacarbonyls,⁷ it may prove possible to prepare dialkyliron tetracarbonyls, $R_2Fe(CO)_4$, derived from iron hydrocarbonyl. However, a tricarbonyl $R_2Fe(CO)_3$ such as (I) would have only 34 electrons about the iron atom and would most probably be paramagnetic, whereas butadieneiron tricarbonyl is diamagnetic.

Further, we have shown that ozonolysis of this compound yields some formaldehyde and that reduction by lithium aluminium hydride yields some butadiene. Although these observations could be explained by the assumption that complete rupture of (I) to yield butadiene is the first step in each case, they are much more consistent with formulations in which the conjugated diene system remains essentially intact. This view is confirmed by the spectra of butadieneiron tricarbonyl. Its ultraviolet spectrum has an intense maximum at 211 $m\mu$ (in ethanol) compared with the maximum of butadiene gas at 217 $m\mu$.⁸ Its infrared spectrum includes a band at 1464 cm^{-1} which may be analogous to the band occurring at 1475 cm^{-1} in the spectrum of the bridged butadiene-platinum complex $K_2[C_4H_6(PtCl_3)_2] \cdot H_2O$ and attributed to a C=C stretching frequency lowered by conjugation and co-ordination to the metal.⁹

We believe that the rejection of structure (I) leaves only one reasonable arrangement for the molecule, *i.e.*, that in which the hydrocarbon attains a planar (or nearly planar) configuration and in which the π -electrons are utilised in bonding. There are two ways of arranging a butadiene molecule in a plane: the "cisoid" form (II) and the "transoid" form (III). To distinguish between these we examined the reaction of iron pentacarbonyl with *cyclohexadiene*. It yields *cyclohexadieneiron tricarbonyl*, almost identical in spectral and other properties with the butadiene compound and therefore presumably analogous in structure. Since *cyclohexadiene* must be cisoid and cannot deviate greatly from planarity, the same arrangement is made highly probable for butadieneiron tricarbonyl. We therefore propose structure (IV) for this compound. In this structure the iron atom lies outside the plane defined by the hydrocarbon portion and is roughly equidistant from the four carbon atoms of the butadiene; the iron atom probably forms a tetrahedron with the three carbonyl groups. It is hoped to confirm this molecular geometry by means of the X-ray crystallographic studies now in progress.



The nature of the bonding between the iron atom and the conjugated diene must be considered, bearing in mind the distribution of the π -orbitals over all four carbon atoms of the latter as the arrangement of lowest energy. We believe that this will lead to a metal-carbon bond of a type more closely related to that in ferrocene,¹⁰ in the benzene-metal compounds (such as dibenzenechromium¹¹ and dimesityleneferrous salts¹²), and that postulated for the hypothetical *cyclobutadiene-metal* compounds,¹³ than to that in

⁸ Smakula, *Angew. Chem.*, 1934, **47**, 657.

⁹ Chatt and Duncanson, *J.*, 1953, 2939.

¹⁰ Pauson, *Quart. Reviews*, 1955, **9**, 391.

¹¹ Fischer and Hafner, *Z. Naturforsch.*, 1955, **10b**, 665; *Z. anorg. Chem.*, 1956, **286**, 146.

¹² Fischer and Böttcher, *Chem. Ber.*, 1956, **89**, 2397.

¹³ Longuet-Higgins and Orgel, *J.*, 1956, 1969.

the chelate complexes of non-conjugated diolefins such as *cyclooctadiene*.^{14,15} This may account for the existence of butadiene complexes of iron in spite of the fact that neither mono-olefins nor non-conjugated dienes have been found to yield complexes with any of the metals from the first row of Group VIII. Thus, according to our views, the conjugated nature of the diene system is an essential feature for the formation of compounds like butadieneiron tricarbonyl, and unconjugated diolefins would not be expected to form iron derivatives of comparable stability or even of comparable type. This consequence is being tested further, as is also the ability of the other transition metals to yield analogous compounds.

The successful preparation of a *cyclohexadieneiron* tricarbonyl suggested that even *cyclopentadiene* derivatives might yield analogous compounds provided they bore two substituents on the methylene carbon atom. Two such derivatives were tested, but both reacted with rearrangement of the carbon skeleton. These results are described in the following paper.

Several attempts have also been made to replace either the hydrocarbon or the carbonyl function directly. When the butadiene derivative is heated with *cyclopentadiene*, complete displacement of the former hydrocarbon occurs and *dicyclopentadienyldiiron* tetracarbonyl³ is formed. When however, butadieneiron tricarbonyl is caused to react with *cyclopentadienylsodium* a new product is formed which retains at least one butadiene residue, but which has bands in the infrared carbonyl stretching region very similar to those of *dicyclopentadienyldi-iron* tetracarbonyl. It is thus clearly at least binuclear, with both bridging and non-bridging carbonyl groups. Its complete structure is under investigation.

All attempts to dehydrogenate *cyclohexadieneiron* tricarbonyl to a benzene-iron derivative have failed.

EXPERIMENTAL

Alumina used for chromatography was Spence's Grade H deactivated by exposure to air for 6 hr. Ligroin refers to the solvent of b. p. 40–60°.

Butadieneiron Tricarbonyl.—This was prepared in an autoclave according to the method of Rheilen *et al.*¹ The product crystallised partially during distillation at 48°/0.06 mm. Recrystallisation from ligroin or methanol at –78° afforded pale yellow crystals of butadieneiron tricarbonyl, m. p. 19°.* Infrared max. in the carbonyl stretching region at approx. 2051 and 1978 cm^{-1} ; ultraviolet max. at 211 μ ($\log \epsilon$ 4.36). The magnetic susceptibility was measured in the liquid phase and showed the compound to be diamagnetic with a molar susceptibility of -78.4×10^{-6} c.g.s.u. at room temp. (*ca.* 24°).

Contrary to the reported decomposition,¹ the compound (0.22 g.) dissolved in cold concentrated sulphuric acid (2 ml.) with only very slight evolution of gas, giving a deep red solution. After standing for 2 hr. at room temperature this solution was poured on ice (20 g.), extracted with ether, and the ether solution washed with sodium hydrogen carbonate solution, dried, and evaporated. Distillation of the residue at 76°/20 mm. afforded unchanged tricarbonyl (0.15 g.).

No hydrogen was absorbed when a solution of the carbonyl (0.39 g.) in ethanol (25 ml.) containing Adams platinum oxide catalyst (20 mg.) was stirred in a hydrogen atmosphere.

Both starting materials were largely recovered unchanged when a solution of butadieneiron tricarbonyl (0.97 g.) and maleic anhydride (0.49 g.) in benzene (15 ml.) was kept at room temp. for 6 days and then heated under reflux for 48 hr. Some decomposition of the carbonyl occurred during this period.

Reduction of Butadieneiron Tricarbonyl with Lithium Aluminium Hydride.¹⁶—The carbonyl (0.054 g.) was added at 0° to a solution of lithium aluminium hydride (0.2 g.) in anhydrous

* The crystalline nature of this product was independently observed some years ago by Dr. H. W. B. Reed of Imperial Chemical Industries Limited (personal communication).

¹⁴ Chatt and Venanzi, *Nature*, 1956, 177, 853.

¹⁵ Chatt, Vallarino, and Venanzi, *J.*, 1957, 2496.

¹⁶ Zeiss and Tsutsui, Technical Report No. 4 under Contract No. DA-19-059-ORD-1494 between the Office of Ordnance Research, U.S. Army, and Yale University, June 1955.

tetrahydrofuran (200 ml.), and the mixture stored at 0° for 6 hr. in a tightly stoppered flask. Water (1 ml.) was then rapidly added, and the mixture warmed gently on a water-bath. The temperature was kept just below the b. p., the reaction flask being connected during this period to a trap containing ethanol at -78°. The ultraviolet spectrum of this alcoholic solution showed a strong peak at 219 m μ corresponding in intensity to the presence of *ca.* 1 mg. (7% yield) of butadiene.

Ozonolysis of Butadieneiron Tricarbonyl.—The carbonyl (0.4 g.), dissolved in glacial acetic acid (50 ml.), was treated with a stream of ozone (3.3%; 350 ml. of oxygen per min.) at room temp. for 30 min. The resultant solution was combined with the water (50 ml.) through which the effluent gases had been passed and distilled with steam over zinc dust (2 g.). From the distillate (150 ml.), neutralised with sodium hydroxide, formaldehyde was precipitated as the dimedone derivative (72 mg.).

Attempted Phenylation of Butadieneiron Tricarbonyl.—Only unchanged tricarbonyl (50–60%, isolated by chromatography of the reaction products on alumina) was recovered when this compound (1 g.) was allowed to react with *N*-nitrosoacetanilide (0.82 g.) in cyclohexane (50 ml.) at room temp. (7 hr.) and 50° (1 hr.), or when it (1.94 g.) was treated with benzenediazonium sulphate (from 1 ml. of aniline) in glacial acetic acid (75 ml.) at room temp. (14 hr.).

Reaction of Butadieneiron Tricarbonyl with cyclopentadiene.—The carbonyl (1.94 g.) and cyclopentadiene (5 ml.; freshly distilled) were heated under carbon dioxide in an autoclave at 150° for 5 hr. Chromatography of a benzene solution of the product on alumina and crystallisation from ligroin yielded purple crystals (309 mg.). Although further crystallisation from the same solvent or from aqueous pyridine as well as sublimation under a high vacuum failed to raise the m. p. of this product above 170–172°, its infrared spectrum was identical with that of dicyclopentadienyldi-iron tetracarbonyl and a mixed m. p. with the latter (m. p. 192°) was undepressed (176–180°).

Reaction of Butadieneiron Tricarbonyl with cyclopentadienylsodium.—A solution of the carbonyl (1.94 g.) in tetrahydrofuran (15 ml.) was added to cyclopentadienylsodium prepared from cyclopentadiene (2 ml.) and sodium (0.26 g.) in the same solvent (25 ml.). After being heated under reflux on a steam-bath for 7 hr. in a current of nitrogen, the solution was evaporated *in vacuo* and the residual red oil was partitioned between ether and water. The yellow aqueous layer was very unstable in air and the product contained in it has not yet been characterised. The purple ether layer was evaporated, leaving an oil which was dissolved in a minimum amount of benzene and chromatographed on alumina. Ligroin eluted a yellow oil (0.33 g.), b. p. 62°/17 mm., which decomposed completely when kept in an evacuated desiccator for a few hours. This was followed by a small amount (*ca.* 20 mg.) of a second unstable, orange oil, eluted by the same solvent. A brownish-purple band was then eluted with benzene and, after evaporation of the solvent, the residue, dissolved in acetone, deposited purple crystals (0.41 g.) on addition of ligroin. Recrystallisation from ligroin afforded the pure product, m. p. 97° (decomp.; *vac.*) [Found: C, 53.8, 52.7; H, 4.4, 4.2; O, 16.4, 16.9%; *M*, 377 (cryoscopic in benzene)]. The compound is diamagnetic: $\chi_{\text{mole}} = -124.7 \times 10^{-6}$ c.g.s.u. It has infrared max. in the carbonyl stretching region at approx. 2029, 1971, 1817, and 1764 cm.⁻¹ and ultraviolet max. at 211 and 343 m μ (log ϵ 4.54 and 3.96).

cycloHexadieneiron Tricarbonyl.—*cycloHexa-1:3*-diene (12 g.) and iron pentacarbonyl (20 g.) were heated under carbon dioxide in an autoclave for 24 hr. at 135–140°. The resulting yellow liquid was dissolved in acetone and filtered from insoluble material. After removal of the solvent and of excess of iron pentacarbonyl, *cyclohexadieneiron tricarbonyl* distilled at 96°/12 mm. as a yellow liquid (4.7 g.), f. p. 8–9° (Found: C, 50.5, 50.3; H, 4.2, 4.0; O, 21.8, 21.9. C₉H₈O₃Fe requires C, 49.1; H, 3.7; O, 21.8%). Infrared max. in the carbonyl stretching region at approx. 2066 and 1978 cm.⁻¹; ultraviolet max. at 207 m μ (log ϵ 4.36). The consistently high C and H analyses obtained for this compound presumably result from difficulty in separating it completely from excess of cyclohexadiene; they are, however, far below those expected for a 2 : 1 ratio of hydrocarbon : iron as found with isoprene and dimethylbutadiene.¹

The authors are indebted to Dr. H. W. B. Reed of I.C.I. Ltd. for supplies of butadiene. They are grateful to Dr. H. Geyer for performing the oxygen analyses. They thank the University of Sheffield for the award of a Henry Ellison Fellowship (to B. F. H.).