

was irrigated successively with water and stepwise increasing concentrations of aqueous ethanol. No glucose was obtained, but maltose was eluted with 7.5% ethanol and maltotriose with 15% ethanol. The appropriate fractions were combined, evaporated to dryness, and dissolved in water for measurement of yield (by acid hydrolysis),  $[\alpha]_D$ , reducing power, and  $\beta$ -amylolysis limits. Portions of the solutions were evaporated to dryness and the solid residues acetylated with sodium acetate-acetic anhydride. The maltotriose acetate was obtained crystalline only after fractionation on Magnesol-Celite (cf. ref. 15). The reducing powers of the two sugars were identical with those of corresponding authentic specimens. Other properties of the isolated maltose and maltotriose were:  $[\alpha]_D$  in  $H_2O$ , +141°, +158°;  $\beta$ -amylolysis limits, 0%, 98%; m. p. of acetate 160°, 136°;  $[\alpha]_D$  of acetate in  $CHCl_3$ , +63°, +87°.

We thank Dr. T. J. Schoch for the waxy-maize starch, Dr. A. K. Balls for the crystalline  $\beta$ -amylase, and the Department of Scientific and Industrial Research for a maintenance grant (to G. J. T.).

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.  
THE LISTER INSTITUTE, LONDON, S.W.1.

(Received, January 6th, 1956.)

<sup>15</sup> Whelan and Roberts, *J.*, 1953, 1298.

### 588. Ferrocene Derivatives. Part III.\* cyclopentadienyliron Carbonyls.

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

Dicyclopentadienyldi-iron tetracarbonyl has been employed as the starting material for two new routes to unsymmetrically substituted ferrocene derivatives. One route proceeds by way of derivatives of dicyclopentadienyliron dicarbonyl, a substance in which only one of the cyclopentadienyl rings is symmetrically bonded to the iron atom. The structure of this compound is proved unambiguously and is discussed in relation to current theories concerning the bonding in compounds of the ferrocene type.

The preparation of dicyclopentadienyldi-iron tetracarbonyl has been described<sup>1,2</sup> and its structure (I) has been established by X-ray crystallography.<sup>3,3</sup> Dicyclopentadiene has hitherto been used in this preparation since it is then possible to carry out the reaction at atmospheric pressure. This procedure suffers from two disadvantages, namely, the decomposition of iron pentacarbonyl at the temperature of the reaction (135°) and the necessity of employing a large excess of hydrocarbon which is difficult to remove from the final product but is necessary to ensure the generation of sufficient cyclopentadiene monomer for the reaction. These disadvantages have now been overcome by using monomeric cyclopentadiene in a closed system. The yield has been raised from 60 to 78% and according to a patent,<sup>4</sup> which became available after the completion of this work, almost quantitative yields have been attained on a large scale. Moreover, the quality of the crude product is much improved and, unlike the earlier method, this variant also affords high yields of the tetracarbonyl (I) when iron enneacarbonyl is used in place of iron pentacarbonyl.

The tetracarbonyl decomposes at about 220°, with the formation of ferrocene. This reaction is promoted<sup>4</sup> at a lower temperature by hydrocarbon solvents and the yield is increased somewhat by the addition of cyclopentadiene. However, the maximum yield claimed (43% based on Fe, 86% based on the cyclopentadiene) is insufficient to establish that additional cyclopentadiene enters directly into the reaction. This is shown conclusively

\* This paper was presented at a meeting of the Chemical Society held at Burlington House on December 15th, 1955. Part II, *J.*, 1955, 367.

<sup>1</sup> Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, 1, 165.

<sup>2</sup> Hallam, Mills, and Pauson, *ibid.*, p. 313.

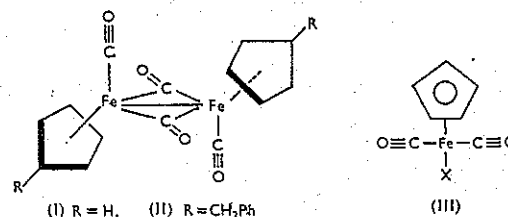
<sup>3</sup> Mills, unpublished work.

<sup>4</sup> Leedham (to Shell), B.P. 737,124; this patent refers to compound (I) as  $(C_5H_5)_2Fe_2(CO)_4$ .

by the successful preparation of unsymmetrically substituted ferrocene derivatives by heating dicyclopentadienyldi-iron tetracarbonyl (I) with substituted cyclopentadienes. Both benzylferrocene and 1:3-diphenylferrocene have been obtained thus, but at reaction the tetracarbonyl (I) with the benzylcyclopentadiene<sup>5</sup> and 1:3-diphenylcyclopentadiene<sup>6</sup> respectively. The method appears to be general and avoids the tedious separation from symmetrically substituted products necessary when a mixture of cyclopentadiene derivatives is used in the Grignard method.<sup>7</sup>

To extend this method to unsymmetrical ferrocene derivatives in which both rings bear substituents, it is necessary to prepare substituted analogues of the cyclopentadiene compound (I). This was attempted with 1:3-diphenylcyclopentadiene, but at reaction temperatures of 150° and 125°, only 1:3:1':3'-tetraphenylferrocene<sup>7</sup> was obtained. This is contrary to patent claims<sup>4</sup> and indicates that the expected bis(diphenylcyclopentadienyldi-iron tetracarbonyl, if formed at all, must decompose under very much milder conditions than the unsubstituted compound. As none of this intermediate could be found, even at the lower temperature (the compound would be expected to be highly coloured and therefore detectable in minute amounts), it appears probable that its formation is prevented, perhaps by steric factors. By contrast, benzylcyclopentadiene reacts with iron pentacarbonyl, under the same conditions as cyclopentadiene itself, to yield the dibenzyl analogue (II). This compound, when strongly heated under reduced pressure, decomposed to dibenzylferrocene identical with a specimen synthesised from benzylcyclopentadienyl-lithium and tetrapyrrolium ferrous chloride.

As previously reported,<sup>1,2</sup> dicyclopentadienyldi-iron tetracarbonyl (I) is oxidised by air in mineral acid solution to form the cyclopentadienyliron dicarbonyl halides (III; X = Cl or Br). This oxidation has also been carried out in perchloric and in sulphuric acid but then no crystalline salt was isolable. It was noted, however, that when a solution of the sulphate, so prepared, was treated with barium chloride, filtered from barium sulphate, and immediately extracted with chloroform, it did not yield the expected product (III; X = Cl). This product was, however, extracted from the aqueous solution several hours later. The slow formation of the chloride (III; X = Cl), which occurred under



these conditions is most readily understood if the product is considered to exist in solvated form in its ionised salts, e.g., as  $[C_5H_5Fe(CO)_2(OH_2)]^+X^-$ , from which the chloride (III; X = Cl) is formed by slow replacement of bound solvent by halogen. This observation throws doubt on the existence<sup>1</sup> of the free ion  $C_5H_5Fe(CO)_2^+$ , which, unlike the postulated solvated form, cannot attain eighteen outer-orbital electrons about the iron atom.

For the preparation of larger quantities of the bromide (III; X = Br) direct oxidation of the tetracarbonyl (I) with bromine was a simpler procedure and gave a higher yield. Analogous preparations of the iodide have recently been described;<sup>8,9</sup> this had previously been obtained<sup>2</sup> by halogen exchange with the chloride, as described on p. 3034.

On treatment with sodium phenylacetylide<sup>2</sup> or with phenyl-lithium the halides (III)

<sup>5</sup> Alder and Holzrichter, *Annalen*, 1936, 524, 146.

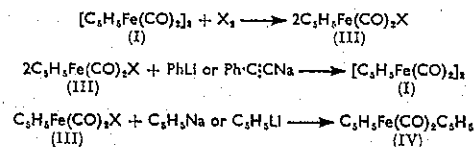
<sup>6</sup> Drake and Adams, *J. Amer. Chem. Soc.*, 1939, 61, 1326.

<sup>7</sup> Part 1, *J. Amer. Chem. Soc.*, 1954, 76, 2187.

<sup>8</sup> Fischer, *Angew. Chem.*, 1955, 67, 476.

<sup>9</sup> Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, 2, 38.

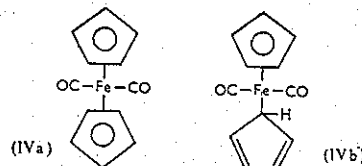
were reduced back to the dicyclopentadienyldi-iron tetracarbonyl (I). In contrast, treatment of these halides (III) with cyclopentadienylsodium or cyclopentadienyl-lithium yielded, in addition to this tetracarbonyl and ferrocene, a compound with the composition of a



dicyclopentadienyliron dicarbonyl (IV).<sup>10</sup> It was natural to assume that this difference in behaviour resulted from the ability of the additional cyclopentadienyl group to be bonded as in ferrocene. The assumption also rested on the theory<sup>11</sup> which postulates only a single  $d_{z^2}$  bond from the central metal atom to each cyclopentadienyl ring in ferrocene and related compounds, so that the iron atom may be regarded as having ten outer-orbital electrons in ferrocene and fourteen in all the above cyclopentadienyliron carbonyl compounds. A structure for dicyclopentadienyliron dicarbonyl (IV), in which both cyclopentadienyl rings are considered to be bonded to iron as in ferrocene, is difficult to account for on the alternative theoretical views of Ruch and Fischer,<sup>12</sup> who have always maintained that the metal atom attains the same number of electrons as the next inert gas in compounds of this type.

While reaffirming the "14-electron theory," Piper and Wilkinson<sup>13</sup> nevertheless proposed that one of the rings in the dicarbonyl (IV) and in an analogous dicyclopentadienylchromium dinitrosyl, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cr(NO)<sub>2</sub>, is linked through a single carbon atom to the metal atom by a normal covalent bond (structure IVb).<sup>\*</sup> Although in the case of the chromium compound analogous methyl and phenyl derivatives, C<sub>5</sub>H<sub>5</sub>CrR(NO)<sub>2</sub> (R = Me or Ph) were reported, no explanation of the formation of only a  $\sigma$ -type bond in the case of the cyclopentadienyl compound was offered. On the basis of the "14-electron theory" it would be expected that the inherently more stable resonating single bond would be formed (structure IVa), especially as both types of bond would utilise the same  $d$  orbitals of the metal.

Structure (IVb) would clearly be the preferable structure on the alternative theory<sup>12</sup> which necessitates the use of three metal orbitals for "ferrocene type" bonding of one



cyclopentadienyl ring, leaving insufficient metal orbitals for similar bonding of the second ring.

In view of these theoretical implications, it appeared desirable to provide more conclusive evidence for one or other of the structures (IVa and b). The latter structure was postulated mainly on the basis of the (rather weak) absorption band observable in the

\* The double bonds in this formula are shown in arbitrary positions. No evidence is available to distinguish between the alternative positions, and only one of the three possible isomers has been isolated.

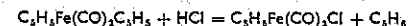
<sup>10</sup> Hallam and Pauson, *Chem. and Ind.*, 1955, 653.

<sup>11</sup> Moffitt, *J. Amer. Chem. Soc.*, 1964, **76**, 3386.

<sup>12</sup> Ruch and Fischer, *Z. Naturforsch.*, 1952, **7b**, 876; Ruch, *Sitzungsber. Bayer. Akad. Wiss., München, math.-naturwiss. Kl.*, 1954, 347; Ruch, *Z. phys. Chem. (Frankfurt)*, 1956, **6**, 356.

<sup>13</sup> Piper and Wilkinson, *Chem. and Ind.*, 1955, 1296.

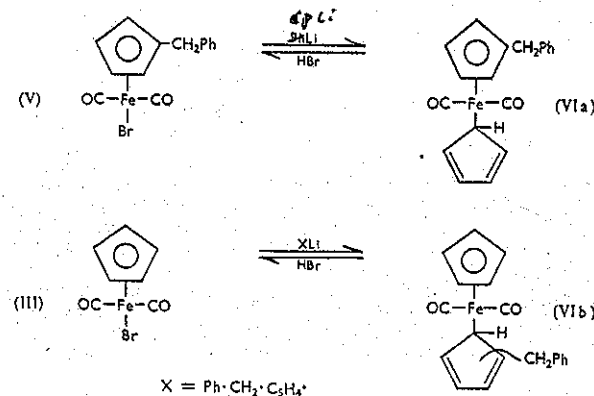
C-H stretching region below 3000 cm.<sup>-1</sup> and attributed to the "aliphatic" C-H bonds in structure (IVb). Several arguments could be adduced in favour of the alternative (IVa), most notably, the gradual decomposition into ferrocene which the compound undergoes at room temperature, even in the solid state. However, when this compound (IV) was heated above its melting point in an attempt to accelerate its decomposition, dicyclopentadienyldi-iron tetracarbonyl (I) was formed in addition to ferrocene; in fact the tetracarbonyl appeared to be the major product of decomposition at 80–100°. Further, dicyclopentadienyliron dicarbonyl is very rapidly hydrolysed by hydrochloric acid, regenerating the chloride (III; X = Cl), presumably according to the equation:



Both these reactions indicate that one cyclopentadienyl ring is more labile than would be expected on the basis of structure (IVa).

Finally, structure (IVb) was conclusively proved by a study of benzyl analogues. Whereas structure (IVa) leads to only one monosubstituted derivative, structure (IVb) leads to different derivatives depending on which ring bears the substituent (*e.g.*, VIa and b). The additional position isomers which arise in the case of (VIb) need not be considered in this connection.

The existence of at least two monosubstituted derivatives was shown in the following way. Di(benzylcyclopentadienyl)di-iron tetracarbonyl (II) was oxidised with bromine in chloroform to benzylcyclopentadienyliron dicarbonyl bromide (V) which was then treated with cyclopentadienyl-lithium to yield the isomer (VIa). Cyclopentadienyliron dicarbonyl bromide (III; X = Br) was treated with benzylcyclopentadienyl-lithium to afford the isomer (VIb). Both of the products (VIa and b) were obtained as oils and, in view of their instability, complete purification was not attempted. They were, however, readily separated from any unchanged starting material and from the by-products (II and I respectively) by chromatography on alumina. Both products exhibited carbonyl stretching frequencies in the infrared spectrum at the characteristic frequencies of compound (IV),



but their spectra show distinct differences at higher wavelengths. That the products were in fact different, as well as the nature of the difference, was clearly evident from the reactions of each with hydrobromic acid. In both cases, only the ring introduced in the last step of the preparation was split off, the compound (VIa) being quantitatively converted into the pure bromide (V), and the isomer (VIb) into the pure bromide (III; X = Br).

Like the parent (IV), the benzyl analogue (VIb) lost carbon monoxide at room temperature, forming benzylferrocene identical with the product described above. This second route to unsymmetrically substituted ferrocene derivatives appears, on the limited

experience available, to be preferable for alkyl derivatives, while the direct route from the tetracarbonyl (I) and a substituted cyclopentadiene has been used more successfully for aryl derivatives.

In attempts to improve the preparation of dicyclopentadienyliron dicarbonyl, the reaction of cyclopentadienylsodium with the halides,  $\text{Fe}(\text{CO})_4\text{I}_2$ <sup>14</sup> and  $\text{Fe}(\text{CO})_2\text{Cl}_2$ <sup>15</sup> was studied. The former gave the same products as cyclopentadienyliron dicarbonyl chloride in this reaction, but in lower yield, whereas the latter afforded only ferrocene. The possibility of obtaining analogues of (I), (III), or (IV), in which one (or more) carbonyl groups is replaced by triphenylphosphine, has also been studied but the attempted direct replacement of carbon monoxide in the compound (I) or (III) by this reagent led instead to replacement of the cyclopentadiene ring. The product formed was identical with a compound to which Reppe *et al.*<sup>16</sup> have assigned the structure  $(\text{Ph}_3\text{P})_3\text{Fe}(\text{CO})_3$ . However, this simple structure is incompatible with the infrared spectrum of the compound, and further investigation of this point is in progress.

The same product was obtained when  $\text{Ph}_3\text{PFe}(\text{CO})_3$ <sup>16</sup> was heated with cyclopentadiene and again when  $\text{Ph}_3\text{PFe}(\text{CO})_3\text{I}_2$  was treated with cyclopentadienylsodium.

#### EXPERIMENTAL

Ligroin refers to the solvent of b. p. 40–60° throughout this paper. Infrared absorptions were measured in potassium bromide discs unless otherwise stated, ultraviolet absorptions in ethanol (95%).

**Dicyclopentadienyl-iron Tetracarbonyl (I).**—(a) *From iron pentacarbonyl.* Freshly distilled cyclopentadiene (30 g.) and iron pentacarbonyl (45 g.) were placed in a one-litre autoclave with sufficient solid carbon dioxide to displace most of the air. This mixture was heated at 135° for 12 hr. The crystalline mass obtained was washed with ligroin to remove unchanged starting materials and crystallised from aqueous pyridine, affording a product (31.5 g., 78%), m. p. 192° (vac.), infrared max. in the carbonyl stretching region at 1762, 1773, 1945, 1959, 1988, and 2052  $\text{cm}^{-1}$ ; ultraviolet max. at 212, 343, and 598  $\mu$  ( $\log \epsilon$  4.46, 3.95, and 3.16).

(b) *From iron enneacarbonyl.* A charge of cyclopentadiene (2.8 g.) and iron enneacarbonyl (3.64 g.) was heated at 140° for 6 hr. and worked up as above. The yield was 2.1 g. (80%).

**cyclopentadienyliron Dicarbonyl Bromide (III; X = Br).**—(a) *By atmospheric oxidation.* A rapid current of air was drawn through a solution of the tetracarbonyl (I) (1.75 g.) in ethanol (100 ml.), chloroform (50 ml.), and 34% hydrobromic acid (10 ml.) during 4 hr. After evaporation under reduced pressure, the residue was dissolved in chloroform, filtered through a short column of alumina, and again evaporated to small bulk. Addition of ligroin afforded red-brown crystals of cyclopentadienyliron dicarbonyl bromide which, recrystallised from chloroform–ligroin, had m. p. 98–102° (decomp.; in air), 105–107° (vac.) (1.65 g., 65%) (Found: C, 33.1; H, 2.0.  $\text{C}_5\text{H}_6\text{O}_2\text{BrFe}$  requires C, 32.7; H, 2.0%). Infrared max. in the carbonyl stretching region at 1995 and 2049  $\text{cm}^{-1}$ . (b) *By use of bromine.* A solution of bromine (1.4 g.) in chloroform (50 ml.) was added dropwise with stirring during 1 hr. to a solution of the tetracarbonyl (I) (2.72 g.) in chloroform (150 ml.), cooled in ice–salt, under nitrogen. The solution was stirred for a further 2 hr., then washed with aqueous sodium thiosulphate, dried ( $\text{CaCl}_2$ ), and evaporated to small bulk. Addition of ligroin afforded the bromide (3.23 g., 82%), identical in m. p. and mixed m. p. with the product described under (a).

**cyclopentadienyliron Dicarbonyl Iodide (III; X = I).**—A solution of the chloride<sup>1</sup> (III; X = Cl) (0.5 g.) and sodium iodide (1.51 g.) in acetone (20 ml.) was refluxed under nitrogen for 24 hr. After evaporation to dryness *in vacuo* the product was extracted with chloroform and filtered through a short column of alumina. Evaporation to small bulk and addition of ligroin yielded dark brown crystals of cyclopentadienyliron dicarbonyl iodide (0.72 g., 65%), m. p. 117–119° (decomp.; vac.) (Found: C, 27.8; H, 1.8.  $\text{C}_5\text{H}_6\text{O}_2\text{IeI}$  requires C, 27.7; H, 1.7%). Infrared max. in the carbonyl stretching region at 1982 and 2042  $\text{cm}^{-1}$ .

**cyclopentadienyliron Dicarbonyl Sulphate Solution.**—The tetracarbonyl (I) was oxidised as described above for the preparation (a) of the bromide, the hydrobromic acid being replaced by

<sup>14</sup> Hieber and Bader, *Ber.*, 1928, 61, 1717.

<sup>15</sup> Hieber and Wirshing, *Z. anorg. Chem.*, 1940, 245, 35.

<sup>16</sup> Reppe and Schwackendiek, *Annalen*, 1948, 560, 104.

concentrated sulphuric acid (1.5 ml.). Evaporation of the resultant solution left a red gum which dissolved completely in water to give a clear deep red solution. This aqueous solution was adjusted to pH 6 by addition of aqueous barium hydroxide and filtered. Addition of barium chloride solution to the filtrate at once precipitated more barium sulphate. This was filtered off and the clear red filtrate shaken with chloroform at once. The chloroform layer remained almost colourless. Gradually, however, the colour passed from the aqueous into the organic layer. After 6 hr., when the water layer had become almost colourless, the chloroform layer was separated. Evaporation yielded the chloride (III; X = Cl).

**Ferrocene from cyclopentadienyliron Carbonyls.**—When the carbonyl (I) or (III; X = Cl or Br) (100 mg.) was heated in a long glass tube for a few minutes over a free flame, and the product extracted with ligroin and purified by sublimation, ferrocene was obtained (yields: 40, 44, and 66% respectively).

**1:3-Diphenylferrocene.**—1:3-Diphenylcyclopentadiene<sup>6</sup> (1.1 g.) was heated with the tetracarbonyl (I) (1.8 g.) in carbon dioxide for 3 hr. at 170° in an autoclave. A ligroin extract of the product was purified by chromatography, yielding 1:3-diphenylferrocene (250 mg.) as orange needles, m. p. 107° (Found: C, 78.3; H, 5.9.  $\text{C}_{22}\text{H}_{18}\text{Fe}$  requires C, 78.1; H, 5.4%).

**Reaction of 1:3-Diphenylcyclopentadiene with Iron Carbonyl.**—Diphenylcyclopentadiene (2.18 g.) and iron pentacarbonyl (1.5 ml.) were heated under carbon dioxide in an autoclave at 150° for 4 hr. The product was chromatographed in benzene on alumina, the same solvent being used as eluant. A small first fraction, largely unchanged hydrocarbon, was followed by a brown band. This was eluted, the benzene removed, and the residue dissolved in a little hot acetone. On cooling 1:3:1':3'-tetraphenylferrocene (250 mg.) separated as orange crystals, m. p. 219–220°, undepressed on admixture with an authentic specimen.<sup>7</sup> No other products were detected in this, or in another experiment conducted at 125°.

**Preparation of Dicyclopentadienyliron Dicarbonyl (IVb).**—A solution of cyclopentadienylsodium was prepared by adding freshly distilled cyclopentadiene (0.5 ml.) to sodium (0.12 g.) under tetrahydrofuran (25 ml.) in nitrogen. The bromide (III; X = Br) (1.29 g.) was added and the mixture stirred for 1 hr. at room temperature. The residue after removal of the solvent under reduced pressure was chromatographed in benzene on alumina (Spence's "Grade H," deactivated by exposure to air for 6 hr.). When benzene was the eluant, an orange-yellow band was rapidly separated from a strongly adsorbed dark brown band. From the latter the tetracarbonyl (I) (15–20% yield) was isolated by extrusion of the column and extraction with acetone. The benzene solution was evaporated and the residue subjected to further chromatography with ligroin as solvent. A pale yellow band containing ferrocene (6–10% yield) was followed by the orange band containing dicyclopentadienyliron dicarbonyl<sup>10</sup> (15% yield). These yields were essentially unaffected by inverting the order of addition of the bromide to the cyclopentadienylsodium. Analogous results were obtained when the bromide (III; X = Br) was replaced by an equivalent amount of the chloride (III; X = Cl), and also when cyclopentadienyl-lithium (prepared from cyclopentadiene and phenyl-lithium) replaced the sodium derivative. Use of excess of the latter reagent increased the yield of ferrocene at the expense of the dicarbonyl (IVb).

**Dicyclopentadienyliron dicarbonyl (IVb)** crystallises readily from ligroin at –70° as orange-red plates, m. p. 46°. It is diamagnetic. Ultraviolet max. are at 211, 320, and 596  $\mu$  ( $\log \epsilon$  4.36, 3.9, and 2.99). Infrared max. are observed in the carbonyl stretching region at 1954 and 2031  $\text{cm}^{-1}$ . Samples kept for several weeks in ordinary specimen tubes, but protected from light, decomposed more or less completely to ferrocene, together with only a small amount of brown insoluble material. At 90° rapid decomposition ensued but only a trace of ferrocene sublimed. The binuclear carbonyl (I) was readily extracted from the residue by acetone.

When the dicarbonyl (IVb) (250 mg.) dissolved in ligroin (25 ml.), was stirred under nitrogen with de-aerated constant-boiling hydrochloric acid (20 ml.), the colour passed from the organic to the aqueous layer within a few minutes. After 40 minutes' stirring to ensure complete reaction the aqueous layer was separated and extracted with several portions of chloroform. The combined extracts were washed with sodium hydrogen carbonate solution, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated *in vacuo* to small bulk. Addition of ligroin precipitated reddish-brown crystals of cyclopentadienyliron dicarbonyl chloride (III; X = Cl) (150 mg., 68%), m. p. and mixed m. p. 84–87°.

**Reaction of Iron Dicarbonyl Dichloride with cyclopentadienylsodium.**—When a tetrahydrofuran solution of cyclopentadienylsodium, prepared as above, was added to iron dicarbonyl dichloride<sup>13</sup> carbon monoxide was rapidly evolved. This was not prevented by cooling in solid carbon dioxide and acetone, and ferrocene (43%) was the only product isolated after working up as in the preparation of the dicarbonyl (IVb).

**Benzylcyclopentadiene.**—This was prepared in good yield by the method given for *n*-pentylcyclopentadiene,<sup>17</sup> by adding benzyl chloride (1 mol.) to a solution of cyclopentadienylsodium [prepared by adding cyclopentadiene (1.2 mols.) to sodamide (from 1 g.-equiv. of sodium) in liquid ammonia]. After removal of solvent, the residue was treated with ice, extracted with ether, dried, and distilled, the fraction of b. p. 115–125°/15 mm.,  $n_D^{20}$  1.5537, being collected (Alder and Holzrichter<sup>8</sup> give b. p. 115–120°/13 mm.). Benzylcyclopentadiene polymerises on storage and was always redistilled (depolymerised) immediately before use.

**Di(benzylcyclopentadienyl)di-iron Tetracarbonyl.**—Benzylcyclopentadiene (10.5 g.) and iron pentacarbonyl (15 g.) were heated in carbon dioxide in an autoclave for 4 hr. at 125–130°. The crystalline product was separated from unchanged starting materials and recrystallised from acetone by addition of ligroin. Di(benzylcyclopentadienyl)di-iron tetracarbonyl formed purple crystals, m. p. 151° (vac.) (4.74 g., 27%) (Found: C, 63.0, 63.3; H, 4.3, 4.1; O, 12.2.  $C_{28}H_{22}O_4Fe_2$  requires C, 63.0; H, 4.2; O, 12.0%).

1:1'-Dibenzylferrocene.—(a) The above product (II) (200 mg.) was heated at 180°/20 mm. for 90 min. Carbon monoxide was evolved and extraction of the black residue with ligroin yielded 1:1'-dibenzylferrocene (76 mg.) as yellow crystals, m. p. 102° (from ligroin) (Found: C, 78.5; H, 5.9.  $C_{22}H_{18}Fe$  requires C, 78.7; H, 6.1%). (b) To a solution of benzylcyclopentadienyl-lithium prepared in ether [from benzylcyclopentadiene (3 g.) and methyl-lithium (0.02 mole)] was added tetrapyrindinium ferrous chloride (4 g.) and tetrahydrofuran (5 ml.). The mixture was stirred at room temperature overnight and then poured into cold dilute hydrochloric acid to precipitate the product. This was purified by chromatography on alumina with ligroin as solvent and was identical in m. p. and mixed m. p. with the product described above.

**Benzylcyclopentadienyliron Dicarboxyl Bromide (V).**—To a stirred solution of the tetracarbonyl (II) (1.07 g.) in chloroform (40 ml.) under nitrogen, a solution of bromine (0.32 g.) in chloroform (20 ml.) was added dropwise during 20 min., with ice-salt cooling. Stirring of the cooled solution was continued for 3 hr. Most of the solvent was evaporated, and ligroin added, yielding red crystals of benzylcyclopentadienyliron dicarbonyl bromide (1.16 g., 83%), m. p. 82° (from chloroform-ligroin) (Found: C, 48.4; H, 3.1.  $C_{14}H_{11}O_2BrFe$  requires C, 48.5; H, 3.2%).

**Reaction of the Bromide (V) with cyclopentadienyl-lithium.**—The bromide (V) (2.25 g.) was added to a stirred suspension of an equimolecular amount of cyclopentadienyl-lithium (prepared from cyclopentadiene and phenyl-lithium in ether (15 ml.) under nitrogen. Tetrahydrofuran (5 ml.) was then added dropwise during 30 min. Stirring was continued for a further 3 hr. After removal of the solvents under reduced pressure the oily residue was dissolved in a small volume of benzene. On chromatography the solution was readily separated into an orange, weakly adsorbed band and a strongly adsorbed brown band, both of which were eluted with benzene. The solution obtained from the brown band on evaporation yielded the tetracarbonyl (II) (0.85 g.). The eluate of the orange band was evaporated to dryness, and the residue dissolved in ligroin and again subjected to chromatography to separate a small yellow band affording crystals of m. p. 72°, presumably benzylferrocene (5 mg.), from the main orange band which was eluted with ligroin and evaporated to give the  $\pi$ -benzylcyclopentadienyl- $\sigma$ -cyclopentadienyliron dicarbonyl (VIa) (200 mg.) as a red oil which failed to crystallise at -78°. A thin film of the oil spread on a rock-salt plate had infrared absorption max. in the carbonyl stretching region at 2007 and 1958  $cm^{-1}$ .

When this oil (200 mg.) was redissolved in ligroin (30 ml.) and stirred under nitrogen at room temperature for 1 hr. with 35% aqueous hydrobromic acid (25 ml.) the colour passed completely into the aqueous layer. The product was extracted into chloroform, washed with sodium hydrogen carbonate solution, dried ( $Na_2SO_4$ ), and evaporated to small bulk. On addition of ligroin and cooling, red crystals of benzylcyclopentadienyliron dicarbonyl bromide (V) (150 mg.), m. p. 78–80°, separated. A single recrystallisation from chloroform-ligroin raised the m. p. to 79–81°, alone or mixed with an authentic specimen.

**Reaction of cyclopentadienyliron Dicarboxyl Bromide (III; X = Br) with Benzylcyclopentadienyl-lithium.**—Benzylcyclopentadiene (2.34 g.) was added to an ether solution (50 ml.) containing an equivalent amount of phenyl-lithium, under nitrogen. To the resulting suspension of benzylcyclopentadienyl-lithium the bromide (III; X = Br) (3.87 g.) was added, followed by a mixture of ether (15 ml.) and tetrahydrofuran (5 ml.) dropwise with stirring during 1 hr. After a further 2 hours' stirring the products were worked up as in the previous experiment. Besides small quantities of the tetracarbonyl (II) and benzylferrocene,  $\sigma$ -benzylcyclopentadienyl- $\pi$ -cyclopentadienyliron dicarbonyl (VIb) (~200 mg.) was obtained as a dark red oil, freezing

<sup>17</sup> Hobbs (to Du Pont), B.P. 733,120.

to orange crystals in carbon dioxide-acetone. A film of the oil absorbed at approx. 1992 and 1941  $cm^{-1}$  in the carbonyl stretching region. This substance decomposed slowly in air. When treated with hydrogen bromide as in the previous experiment, it yielded almost quantitatively the bromide (III; X = Br), m. p. 98–100° raised by one crystallisation to 102–104° undepressed on admixture with an authentic specimen.

**Benzylferrocene.**—(a) The dicarbonyl (VIa), kept in air at room temperature for 4 days, decomposed completely. The ligroin-soluble fraction was chromatographed on alumina and yielded, apart from a small strongly adsorbed band which appeared to contain the tetracarbonyl (II) (but in insufficient quantity to permit isolation in a pure state), only a single yellow band from which benzylferrocene was readily obtained on elution with ligroin. The yellow crystals had m. p. 76°, undepressed on admixture with the product described below.

(b) A mixture of dicyclopentadienyldi-iron tetracarbonyl (I) (3.54 g.) and benzylcyclopentadiene (6.24 g.) was heated in an autoclave at 170° for 3 hr. in carbon dioxide. The dark oily product was passed through an alumina column in benzene solution, and a yellow oil was recovered on evaporation of the solvent. This oil contained unchanged hydrocarbon and was separated by shaking its ether solution with benzoquinone and concentrated hydrochloric acid in order to convert the desired product into benzylferricinium chloride which passed into the aqueous layer. This was separated and immediately reduced back by addition of aqueous titanous sulphate. Extraction with ether and evaporation afforded the regenerated benzylferrocene, m. p. 76° (Found: C, 73.8; H, 5.9.  $C_{17}H_{12}Fe$  requires C, 73.9; H, 5.8%).

**Triphenylphosphine-iron Tricarbonyl Iodide.**—Iron tetracarbonyl iodide<sup>18</sup> evolves only 1 mol. of carbon monoxide when treated with excess of triphenylphosphine at room temperature. It is known<sup>18</sup> that only one carbonyl group is replaced by triphenyl phosphite under comparable conditions. To the iodide (4.22 g.), dissolved in the minimum quantity of ether, triphenylphosphine (2.62 g.) in ether was added dropwise during 30 min. with stirring. When gas evolution appeared complete (ca. 90 min.) the solvent was evaporated at room temperature. Triphenylphosphine-iron tricarbonyl iodide was obtained as reddish-brown crystals (6.1 g., 93%) which were recrystallised from benzene-ligroin or, preferably, acetone-water. It decomposes without melting above 116° and slowly evolves carbon monoxide in solution. Hence a completely pure sample was not obtained on crystallisation (Found: C, 39.4; H, 2.8. Calc. for  $C_{21}H_{15}O_3I_2PF_6$ : C, 38.5; H, 2.3%).

When this product (2.19 g.) in tetrahydrofuran (20 ml.) was added to cyclopentadienylsodium (from 0.48 g. of cyclopentadiene and 0.17 g. of sodium) in tetrahydrofuran (15 ml.) under nitrogen some gas was evolved. The mixture was stirred for 45 min., then the solvent was removed *in vacuo* and the benzene-soluble portion of the product chromatographed on alumina. A single pale green band was obtained from which bistrisphenylphosphineiron tricarbonyl,<sup>18</sup> m. p. and mixed m. p. 287° (vac.), was obtained on elution with benzene and crystallisation from the same solvent.

This product also resulted when triphenylphosphine was heated in an autoclave with an equimolecular amount of the tetracarbonyl (I) for 4 hr. at 170° or with the chloride (III) for 3 hr. at 120°, or when triphenylphosphineiron tetracarbonyl was similarly heated with cyclopentadiene for 4 hr. at 170°.

The authors are indebted to the University of Sheffield for the award of a Henry Ellison Fellowship to B. F. Hallam.

CHEMISTRY DEPARTMENT, THE UNIVERSITY,  
SHEFFIELD, 10.

[Received, March 29th, 1956.]

<sup>18</sup> Reed, *J.*, 1954, 1931.