126. *Ferrocene Derivatives. Part IV.*[1] *Indenyl- and Tetrahydroindenyl-iron Carbonyls.*

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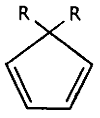
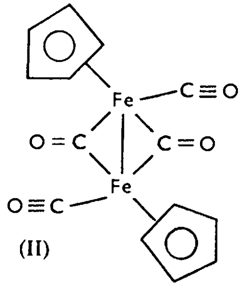
The structures of *spiro*[2 : 4]hepta-1 : 3-diene and *spiro*[4 : 4]nona-1 : 3-diene have been confirmed. Both hydrocarbons rearrange during their reactions with iron pentacarbonyl. The *spiro*nonadiene yields bistetrahydroindenyldi-iron tetracarbonyl (VII), which is converted by pyrolysis into bistetrahydroindenyliron. Indene reacts with iron pentacarbonyl to yield di-indenyldi-iron tetracarbonyl which has been reduced to the same tetrahydro-derivative (VII).

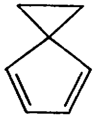
IN connection with the study of butadieneiron tricarbonyl (preceding paper) it appeared of interest to determine whether 5 : 5-disubstituted *cyclo*pentadienes (I) would give analogous products with iron pentacarbonyl. The reaction occurs (with butadiene and related dienes) under conditions under which *cyclo*pentadiene itself yields di*cyclo*pentadienyldi-iron tetracarbonyl (II) [1] in which the metal–ring bonding is of the ferrocene type. This cannot be attained with the *gem.*-disubstituted derivatives (I) (except with rearrangement of the carbon skeleton). Hence it might be expected that *cyclo*pentadienes of this type (I) would form products having the (presumably less energetically favourable) type of bonding found in the butadiene complex. In practice this expectation was not realised, the two compounds studied, *spiro*[2 : 4]hepta-1 : 3-diene (III) [2] and *spiro*[4 : 4]nona-1 : 3-diene (IV),[3] reacting exclusively with rearrangement to yield binuclear tetracarbonyls analogous to (II).



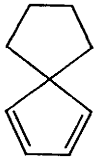
(I)



(II)



(III)



(IV)

The spirans (III) and (IV) were selected because, among the few known simple *gem.*-disubstituted *cyclo*pentadiene derivatives, they appeared most readily accessible, being obtained by direct alkylation of *cyclo*pentadiene, without danger of contamination from lower or higher homologues. Unfortunately, however, their structures—particularly that of (IV)— had not previously been rigidly established and it was therefore necessary to do this by degradative methods. The *spiro*nonadiene (IV) is obtained by reaction of *cyclo*pentadiene with sodamide and tetramethylene bromide in liquid ammonia. This alkylation must proceed in two stages. The first reaction of the dihalide with *cyclo*pentadienylsodium leads to the intermediate (Va) which then reacts with more sodamide to yield its salt (Vb). As the negative charge in the latter is not localised on any particular ring carbon atom, it could cyclise either to (IV) or to an isomer having the indene skeleton, *e.g.*, (VI), or to a mixture of the two. The only evidence previously advanced [3] in support of the formulation as (IV) was comparison of the boiling point and refractive index of its tetrahydro-derivative with the data recorded for authentic *spiro*[4 : 4]nonane. Such comparison does not appear to rule out structures such as (VI) for all or part of the material.

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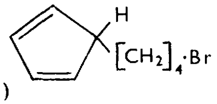
[1] Part III, *J.*, 1956, **3030**.

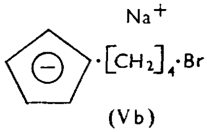
[2] Levina, Mezentsova, and Lebeda, *Zhur. obshchei Khim.*, 1955, **29**, 1097.

[3] Levina and Tantsireva, *Doklady Akad. Nauk S.S.S.R.*, 1953, **89**, 697.

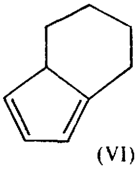
Similarly, no evidence had been presented to rule out alternative structures for (III) and, although in this case the fused *bicyclo*[3 : 2 : 0]heptadiene structure appears *a priori* less likely, it was decided to reinvestigate both compounds. Ozonolysis converted (III) and (IV) into *cyclo*propane-1 : 1-dicarboxylic and *cyclo*pentane-1 : 1-dicarboxylic acids respectively, but in poor yields. In the case of the *spiro*nonadiene (IV), permanganate oxidation gave improved results. Fortunately, the maleic anhydride adducts [2, 3] could be prepared in over 90% yield in both cases, proving the essential homogeneity of the hydrocarbons and hence—in conjunction with the oxidative evidence—that at least 90% of each of the hydrocarbons had the structure assigned to it.



(Va)



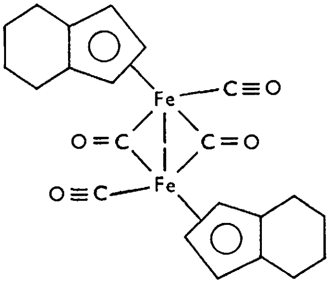
(Vb)



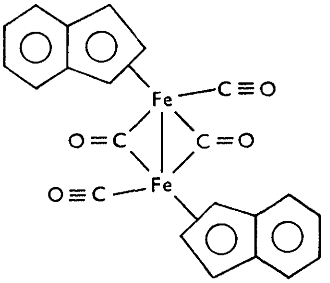
(VI)

When the *spiro*heptadiene (III) was heated with iron pentacarbonyl it afforded mainly a purple gum, resembling the tetracarbonyl (II), but clearly polymeric. A crystalline fraction (1·6%) was identified as the diethyl derivative of (II) by analysis and infrared spectrum. Both products are best understood as resulting from the opening of the *cyclo*propane ring of (III). This would yield mainly vinyl*cyclo*pentadiene and it is here postulated that the major polymeric product is derived from this hydrocarbon. Ethyl*cyclo*pentadiene (or the ethyl*cyclo*pentadienyl radical) can clearly arise by partial disproportionation of the radical intermediate of this ring fission. However, the yield of the crystalline product was too low to exclude the possibility that sufficient ethyl*cyclo*pentadiene for its formation was present in the starting material (III) [as a result of reduction of the intermediate bromoethyl*cyclo*pentadiene during the liquid ammonia reaction].

More clear-cut results were obtained with the *spiro*nonadiene (IV) which reacted with iron pentacarbonyl to give bistetrahydroindenyldi-iron tetracarbonyl (VII) in 39% yield. Since the starting material is at least 91% pure (IV), the formation of (VII) can only be attributed to rearrangement of (IV) during the reaction and not to the possible presence of traces of tetrahydroindenes in the starting material. The possibility remains that this rearrangement of the spiran (IV) occurs independently of its reaction with iron pentacarbonyl. In an attempt to test this, a sample of the hydrocarbon (IV) was heated under the reaction conditions. However, the main product was a new hydrocarbon of double the molecular weight and it is not known whether this is a dimer of the spiran (IV) itself or a dimer of a rearrangement product.



(VII)



(VIII)

The structure of the tetracarbonyl (VII) was proved both by conversion into the known bistetrahydroindenyliron [4] on pyrolysis and by an independent synthesis from indene. The latter reacted with iron pentacarbonyl in the same fashion as *cyclo*pentadiene, yielding di-indenyldi-iron tetracarbonyl (VIII). Surprisingly, this compound is comparable in

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[4] Fischer and Seus, *Z. Naturforsch.*, 1954, **9b**, 386.

stability with its *cyclo*pentadiene analogue (II), whereas di-indenyliron is very unstable compared with ferrocene. This indene compound (VIII) was smoothly hydrogenated to the octahydro-derivative (VII) at room temperature and pressure provided a large excess of platinic oxide catalyst was used. This reduction closely parallels that of di-indenyliron to its octahydro-derivative.[4] The resistance, not only of the *cyclo*pentadiene ring, but of the whole system (II), to these hydrogenation conditions was separately demonstrated before this series of reactions was undertaken. Reduction of (VIII) to (VII) incidentally proves that the indene molecules in (VIII) are linked to the metal atoms through the five-membered and not (as in dimesityleneiron salts [5]) through the benzenoid rings.

The absorption of (VII) in the carbonyl stretching region of the infrared is almost indistinguishable from that of (II), but that of (VIII) shows significant differences, the position of the main bridging carbonyl band being shifted appreciably towards higher wavelength. This observation stresses the extent to which relatively remote parts of a molecule can affect such specific group frequencies.

EXPERIMENTAL

spiro[2 : 4]*Hepta*-1 : 3-*diene*.—Following Levina *et al.*[2] *cyclo*pentadiene (50 g.) was added during 30 min. to a solution of sodium (35 g.) in liquid ammonia (1500 ml.) under reflux. Then 1 : 2-dibromoethane (144 g.) was run in during 40 min., and, after a further 1·5 hours' stirring the reaction mixture was treated with ether (200 ml.) and water (400 ml.). The ether layer, combined with ether extracts of the aqueous layer, was washed with water and dilute hydrochloric acid, dried (Na_2SO_4), and evaporated. Fractional distillation of the residue yielded the *spiro*heptadiene (III) (13·2 g.), b. p. 45—47°/93 mm., n_D^{20} 1·5070 (lit.,[2] b. p. 57°/100 mm., n_D^{20} 1·5078).

This spiran (0·35 g.) reacted exothermically with maleic anhydride (0·37 g.) dissolved in benzene (4 ml.). After standing for 1 hr. at room temp. this solution was evaporated, and the residue crystallised from ether–ligroin (b. p. 40—60°), yielding the adduct (0·65 g.; 90%), m. p. 97—98° (lit.,[2] m. p. 97°).

Ozonolysis of the Spiran (III).—A stream of ozone (3·3%; 350 ml. of oxygen per min.) was passed for 3·5 hr. through a solution of the spiran (III) (2·76 g.) in ethyl acetate (50 ml.) at −78°. Glacial acetic acid (75 ml.) was then added, and the solution evaporated *in vacuo* to approx. 20 ml. It was now added to a mixture of hydrogen peroxide (20 ml.; 100-vol.), concentrated sulphuric acid (0·75 ml.), and water (30 ml.), cautiously warmed to 40°, and kept at this temperature for 1 hr. After standing at room temp. for 36 hr. the solution was evaporated to small bulk under reduced pressure and the residue, acidified with dilute hydrochloric acid, extracted continuously with ether for 24 hr. Evaporation of the dried (Na_2SO_4) ether solution and crystallisation of the residue from chloroform–ligroin (b. p. 40—60°) yielded *cyclo*propane-1 : 1-dicarboxylic acid, m. p. 134—136° (1·33 g.; 34%), undepressed by an authentic specimen; the infrared spectra were identical.

spiro[4 : 4]*Nona*-1 : 3-*diene* (IV).—This spiran was prepared (see Levina *et al.*[3]) like its lower homologue (III) from sodium (20 g.) in liquid ammonia (500 ml.), *cyclo*pentadiene (28 g.), and 1 : 4-dibromobutane (80 g.). The product (IV) (5·7 g.) had b. p. 44—46°/22 mm., n_D^{20} 1·4817 (lit.,[3] b. p. 52°/10 mm.; n_D^{20} 1·4790). A sample (0·20 g.) reacted exothermically with maleic anhydride (0·163 g.) in benzene (2 g.), yielding the adduct as silvery white plates [0·33 g. 91%; from ether–ligroin (b. p. 40—60°)], m. p. 100—101° (lit.,[3] 98°) (Found: C, 71·2; H, 6·8. Calc. for $C_{13}H_{14}O_3$: C, 71·5; H, 6·5%). The m. p. was unchanged on further recrystallisation. The homogeneity was further verified by hydrolysis with 2N-sodium hydroxide (20 ml.) for 1 hr. on a steam-bath; the adduct (0·26 g.) was completely hydrolysed to the corresponding *dicarboxylic acid* (0·277 g.), m. p. 180° (decomp.), isolated by acidification, filtration, and crystallisation from acetone at low temperature (Found: C, 65·7, 65·9; H, 6·7, 6·9. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%). A pure sample of this acid (0·1 g.) was reconverted into the anhydride by refluxing (1·5 hr.) with acetyl chloride (2 ml.), evaporation, and crystallisation from ether–ligroin. The product (83 mg.) had m. p. 98—99°, undepressed by admixture with the original adduct.

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[5] Fischer and Böttcher, *Chem Ber.* 1956, **89**, 2397.

Ozonolysis of the Spiran (IV).—Ozonolysis of the *spiro*nonadiene (IV) (2·4 g.) was carried out for 2·5 hr. under the same conditions as described for the *spiro*heptadiene (III). After addition of the solution of the products in acetic acid (25 ml.) to a mixture of hydrogen peroxide (20 g.), concentrated sulphuric acid (0·5 ml.), and water (20 ml.), the resultant suspension was stirred at room temperature for 18 hr. during which the flocculent white precipitate dissolved. Evaporation *in vacuo* left a mixture of white crystals and colourless oil, which was separated into a neutral and an acidic (hydrogen carbonate-soluble) fraction. The former, a colourless non-ketonic oil (125 mg.), was not further investigated. The acidified hydrogen carbonate solution was extracted continuously with ether (24 hr.), yielding the acidic fraction (after drying and evaporation of the ether solution) as a mixture of crystals and oil (2 g.) which were separated by filtration. The acidic oil liberated iodine from potassium iodide and reacted violently with aniline, but could not be identified. The crystals were dried on porous plate and recrystallised from ether–ligroin (b. p. 40—60°) yielding *cyclo*pentane-1 : 1-dicarboxylic acid (0·31 g.; 10%),m. p. 185° (decomp.); mixed m. p. with authentic specimen (m. p. 189°) 187°. The infrared spectra of the two samples were identical.

Oxidation of the Spiran (IV) *with Potassium Permanganate.*—Finely ground potassium permanganate (12·5 g.) was added in small portions during 1 hr. to a vigorously stirred solution of the *spiro*nonadiene (IV) (1·2 g.) and sodium hydrogen carbonate (0·5 g.) in acetone (50 ml.) and the mixture was stirred overnight, then acidified with dilute sulphuric acid; sulphur dioxide was then passed in until a clear solution was obtained, and this was extracted continuously with ether for 24 hr. The resultant ether solution was extracted with sodium hydrogen carbonate solution, leaving a neutral oil (0·28 g.) in the organic layer. Acidification of the aqueous layer and re-extraction into ether followed by evaporation afforded oily crystals which were dissolved in benzene and precipitated by addition of ligroin, leaving a colourless oil (0·15 g.) in the mother liquors. Recrystallisation of the precipitate from chloroform–ligroin (b. p. 40—60°) afforded *cyclo*pentane-1 : 1-dicarboxylic acid (0·485 g.), m. p. 186° (decomp.), undepressed on admixture with an authentic specimen.

Pyrolysis of the Spiran (IV).—The *spiro*nonadiene (IV) (4 g.) was heated in a sealed tube at 130° for 24 hr. and the resulting yellow liquid was purified by passing its ligroin solution through a column of alumina. Evaporation of the solvent under reduced pressure left a colourless liquid (3·65 g.) which did not react with maleic anhydride, had an apparent molecular weight of 166, 169 (cryoscopic in benzene), and had only extremely weak maxima at 221 and 260 mμ [the latter being less than 2% of the intensity of the maximum at 256 mμ of the starting material (IV)]. Distillation of a portion of this material yielded a small fraction (0·28 g.), b. p. 100—105° (bath temp.)/19 mm. (Found: *M*, 119·5. Calc. for C_9H_{12}: *M*, 120·2), which like the crude product, failed to react with maleic anhydride. The remainder (1·65 g.) distilled from a bath at 110—120°/0·01 mm. and had the molecular weight calculated for a dimer (Found: 230, 234). This fraction was transparent in the ultraviolet region between 205 and 300 mμ.

Reaction of the Spiran (III) *with Iron Pentacarbonyl.*—The *spiro*heptadiene (III) (13 g.) and iron pentacarbonyl (28 g.) were heated under carbon dioxide in an autoclave at 140° for 36 hr. Extraction of the product with a small volume of acetone left a purple chloroform-soluble tar. The acetone solution was evaporated under reduced pressure to remove solvent and unchanged iron pentacarbonyl. The residual red oil was dissolved in the minimum amount of benzene and chromatographed on alumina (see preceding paper). The main purple band was eluted with benzene–ligroin (3 : 2), which, on evaporation, yielded purple crystals [216 mg.; 1·6% based on $Fe(CO)_5$]. Recrystallisation from ligroin afforded *bisethyl*cyclo*pentadienyldi-iron tetracarbonyl*, m. p. 61—62° (decomp.; vac.) (Found: C, 52·9, 53·1; H, 4·6, 4·7. $C_{18}H_{18}O_4Fe_2$ requires C, 52·7; H, 4·4%).

Bistetrahydroindenyldi-iron Tetracarbonyl (VII).—(*a*) *From the spiran* (IV). The *spiro*nonadiene (IV) (8 g.) and iron pentacarbonyl (12 g.) were heated under carbon dioxide in an autoclave at 130° for 25 hr., yielding a purple oil which was dissolved in the minimum amount of benzene and chromatographed on alumina (see preceding paper). The main purple band, eluted from the column with benzene–ligroin (3 : 2), gave, after evaporation of the solvent and addition of ligroin (b. p. 40—60°), purple crystals (6 g.; 39% based on *spiro*nonadiene), leaving an oil (3 g.) in the mother liquors. Recrystallisation of the solid product from ligroin (b. p. 60—80°) afforded *bistetrahydroindenyldi-iron tetracarbonyl* (VII), m. p. 148° (decomp., vac.) (Found: C, 57·2, 57·4; H, 4·9, 4·9. $C_{22}H_{22}O_4Fe$ requires C, 57·2; H, 4·8%). Infrared max. in the carbonyl stretching region at approx. 1951 and 1754 cm.$^{-1}$ (KBr disc).

This tetracarbonyl (VII) was recovered unchanged after its methanol solution had been stirred with hydrogen in the presence of Adams catalyst. A sample of (VII) (0·5 g.) was heated for a few minutes over a free flame and yielded an orange oil which was purified by chromatography on alumina and distillation at 130° (bath temp.)/0·05 mm. This oil was identified as bistetrahydroindenyliron by comparison of its infrared spectrum with that of an authentic specimen prepared by the method of Fischer and Seus.[4]

(*b*) *From di-indenyldi-iron tetracarbonyl* (VIII). To a solution of the tetracarbonyl (VIII) (0·1 g.) in ethanol (25 ml.), Adams catalyst (150 mg.) was added and the mixture was stirred under hydrogen until its uptake ceased (50 ml. at 743 mm. and 19°). Filtration and evaporation to small bulk yielded bistetrahydroindenyldi-iron tetracarbonyl, identical in appearance, m. p., mixed m. p., and infrared spectrum with the above sample.

Di-indenyldi-iron Tetracarbonyl (VIII).—Freshly distilled indene (12 g.) and iron pentacarbonyl (20 g.) were heated together under carbon dioxide in an autoclave at 130° for 24 hr. The crystalline product, separated by filtration from an intractable red oil (6·2 g.), was purified by recrystallisation from chloroform–ligroin (b. p. 40—60°), yielding brownish-purple crystals of *di-indenyldi-iron tetracarbonyl* (VIII) (4·6 g.), m. p. 198° (decomp., vac.) (Found: C, 57·9, 57·6; H, 3·6, 3·5. $C_{22}H_{14}O_4Fe_2$ requires C, 58·2; H, 3·1%). Infrared max. in the carbonyl stretching region at approx. 1951 and 1790 cm.$^{-1}$ (as KBr disc).

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