The 2,4-dinitrophenylhydrazone derivative, prepared in the normal manner, crystallized from ethanol-ethyl acetate solutions in red needles, m.p. 192–193° dec.

Anal. Calcd. for $C_{15}H_{11}O_7N_4Fe$: C, 43.29; H, 2.91; N, 13.46. Found: C, 43.18; H, 2.82; N, 13.70.

***trans-trans*-3,5-Heptadien-2-ol-iron Tricarbonyl from Reaction of Methylmagnesium Iodide with *trans-trans*-2,4-Hexadienaliron Tricarbonyl.**—An ethereal solution of methylmagnesium iodide (prepared from 9.72 g. of magnesium and 39.8 g. of iodomethane) was added slowly to a cooled solution (0°) of 57.0 g. of *trans-trans*-2,4-hexadienaliron tricarbonyl in 1 l. of dry ether. The reaction mixture became very viscous during the addition. The mixture was stirred for 30 min. and hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated and the aqueous solution extracted twice with ether. The combined ether extracts were washed with 5% sodium carbonate and water and then were dried over magnesium sulfate. Removal of the solvent left a thick red oil which was distilled to yield 31.3 g. of complex, b.p. 110–115° (0.3 mm.). An infrared spectrum of the distillate indicated the presence of small amounts of unreacted aldehyde complex. Crystallization of the crude product from pentane yielded the alcohol complex VIII, m.p. 68–70°. Repeated recrystallizations from petroleum ether gave fine yellow needles, m.p. 70–71.5°.

Anal. Calcd. for $C_{10}H_{12}O_4Fe$: C, 47.66; H, 4.80. Found: C, 47.44; H, 4.99.

Repeated crystallization of the material obtained following evaporation of the mother liquors afforded a small amount of the other diastereoisomer of VIII, m.p. 85–86°.

A portion of the isomer, m.p. 70°, was dissolved in light petroleum and chromatographed over alumina. It was found, after solvent removal, that the complex now melted at 85°.

A solution obtained upon dissolving 1.0 g. of the alcohol complex, m.p. 70°, in 20 ml. of 10% fluoroboric acid was diluted with water and extracted with ether. Evaporation of the ether afforded 0.90 g. of alcohol complex, m.p. 85°.

A small portion of the isomer, m.p. 70°, was degraded with ceric ammonium nitrate; gas chromatography indicated that the liberated dienol was the same as the dienol liberated by degradation of the isomer, m.p. 85°.

A comparison of the infrared spectra of the two isomers is given in this Experimental section which describes the reaction of the dimethyl salt with water.

***trans-trans*-3,5-Heptadien-2-ol-iron Tricarbonyl from the Reaction of Iron Pentacarbonyl with *trans-trans*-3,5-Heptadien-2-ol.**—*trans-trans*-3,5-Heptadien-2-ol was prepared by addition of 96.0 g. of *trans-trans*-2,4-hexadienal to methylmagnesium iodide (from 150.0 g. of methyl iodide and 32 g. of magnesium) in 600 ml. of ether. Treatment of the mixture in the usual manner afforded 70.0 g. of product, b.p. 87–90° (25 mm.). The infrared spectrum did not display strong carbonyl absorption.

A solution containing 70.0 g. of crude *trans-trans*-3,5-heptadien-2-ol and 200 g. of iron pentacarbonyl was refluxed gently under nitrogen for 58 hr. After cooling, the volatile materials were removed under reduced pressure and the remaining oil was distilled to yield 35.7 g. of *trans-trans*-3,5-heptadien-2-ol-iron tricarbonyl, b.p. 110–115° (0.3 mm.). The complex became solid upon cooling and several crystallizations from pentane afforded yellow needles, m.p. 85°.

An infrared spectrum of the complex exhibited absorptions at 3425 cm.$^{-1}$ (OH) and 2045, 1979, and 1971 cm.$^{-1}$ ($C\equiv O$).

***syn-syn*-1,5-Dimethylpentadienyliron Tricarbonyl Fluoroborate.**—A solution of 17.8 g. of 40% fluoroboric acid in 90 ml. of propionic anhydride (prepared by adding the aqueous acid to the anhydride cooled in an ice bath) was added slowly to a cooled (0°) solution of 20.0 g. of *trans-trans*-3,5-heptadien-2-ol-iron tricarbonyl (m.p. 85°) in 80 ml. of propionic anhydride. The *syn-syn-1,5-dimethylpentadienyliron tricarbonyl fluoroborate salt* crystallized from the solution and, after stirring for 30 min. at 0°, was filtered, washed with ether, and dried. The salt, 21.4 g., was recrystallized from nitromethane to give yellow needles, which decomposed without melting above 220°.

Anal. Calcd. for $C_{10}H_{11}BO_3F_4Fe$: C, 37.32; H, 3.44; B, 3.36; F, 23.61. Found: C, 37.06; H, 3.59; B, 3.20; F, 23.30.

An infrared spectrum of the salt as a mull in hexachlorobutadiene showed bands at 2111 and 2060 cm.$^{-1}$ ($C\equiv O$).

The n.m.r. spectrum of this salt in liquid sulfur dioxide is shown in Fig. 2 of the text and from this spectrum, the following coupling constants are evaluated: J_{cd} = 7.0; J_{ad} = 11.5–12; $J_{CH_3,a}$ = 6.2 c.p.s.

Treatment of the isomer, m.p. 70°, with fluoroboric acid, in the same manner as before, afforded a 94% yield of *syn-syn*-1,5-dimethylpentadienyliron tricarbonyl fluoroborate.

Reaction of *syn-syn*-1,5-Dimethylpentadienyliron Tricarbonyl Fluoroborate with Water. To 300 ml. of water was added 13.5 g. of *syn-syn*-1,5-dimethylpentadienyliron tricarbonyl fluoroborate. The reaction mixture was stirred for 20 min. and then extracted with pentane. The pentane extracts were washed with water and dried over magnesium sulfate. One crystallization from pentane afforded *trans-trans*-3,5-heptadien-2-ol-iron tricarbonyl as yellow needles, m.p. 83–85°. A second crystallization from pentane gave the pure material (8.0 g.), m.p. 85°.

Anal. Calcd. for $C_{10}H_{12}Fe$: C, 47.66; H, 4.80. Found: C, 47.44; H, 4.97.

The infrared spectrum of this complex, m.p. 85°, is almost identical with that of the isomer melting at 70°; the only differences are the appearance of medium absorption bands at 683 and 1000 cm.$^{-1}$ in the spectrum of the latter compound which are not present in that of the other isomer.

The n.m.r. spectra of the alcohol complex, m.p. 85°, and of the isomer, m.p. 70°, in carbon tetrachloride exhibit absorptions at 4.84, 6.45, 6.87, 8.4, 8.6, and 9.06 τ with respective areas of 2:1:1:1:6:1.

Acknowledgments.—We wish to thank the National Science Foundation and the Robert A. Welch Foundation for financial support. We also thank Antara Chemicals for a generous gift of iron carbonyl.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS]

Organo–Iron Complexes. III.[1,2] Reactions of the *syn*-1-Methylpentadienyliron Tricarbonyl Cation

BY J. E. MAHLER, DOROTHY H. GIBSON, AND R. PETTIT

RECEIVED JUNE 7, 1963

The synthesis and reactions of salts of the *syn*-1-methylpentadienyliron tricarbonyl cation are discussed. A high degree of selectivity is seen in the reactions of the cation with water, alcohols, and zinc dust; it is not seen, however, in the case of sodium borohydride.

As shown in the previous paper the reaction of 2,4-dien-1-ol-iron tricarbonyl complexes with strong acids affords a convenient synthesis of salts of pentadienyliron tricarbonyl cations. In this paper we report the preparation of salts of the *syn*-1-methylpentadienyliron tricarbonyl cation (I) utilizing this method and discuss several chemical reactions of these salts. Reactions of the unsymmetrical cation I could, in principle, lead to a larger number of products than would be expected from the symmetrical systems discussed previously, and it is of interest to determine the degree of selectivity which might be attained in such reactions.

Results and Discussion

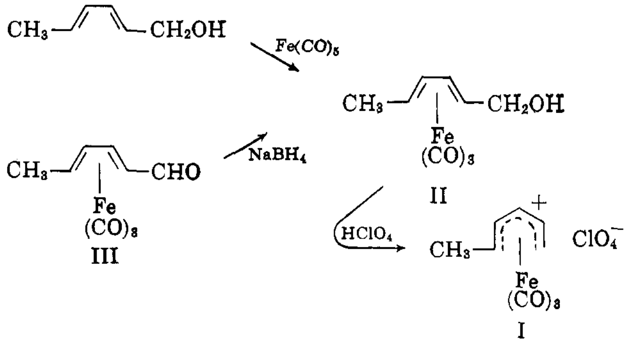
Salts of the *syn*-1-methylpentadienyliron tricarbonyl cation have been prepared by means of the reactions indicated in the scheme shown at the top of the next page.

trans-trans-2,4-Hexadien-1-ol-iron tricarbonyl (II) is prepared through the reaction of 2,4-hexadienol with iron pentacarbonyl; an alternative route is provided by reduction of 2,4-hexadienaliron tricarbonyl (III) with sodium borohydride. Treatment of the alcohol complex with perchloric acid affords *syn*-π-1-methylpenta-

---

[1] Part II: J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

[2] A preliminary account of some of this work has been published: J. E. Mahler and R. Pettit, *ibid.*, **84**, 1511 (1962).



dienyliron tricarbonyl perchlorate in quantitative yields. Other salts such as the fluoroborate and hexafluorophosphate are readily available from the reaction of II with the appropriate acid.

The cation I is also formed, together with triphenylmethanol, through reaction of the alcohol complex with triphenylcarbonium salts. It is not formed, however, upon similar treatment of II with salts of the tropylium cation.

By analogy with the related pentadienyl- and 1,5-dimethylpentadienyliron tricarbonyl cations reported in the previous paper,[1] the five sp^2 carbons of the dienyl ligand in I are assigned the completely cissoid configuration shown. Further direct evidence for this structure is seen in the n.m.r. spectrum given in Fig. 1.

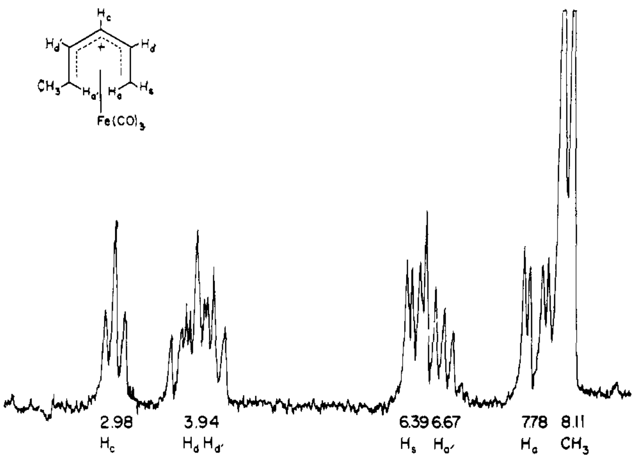
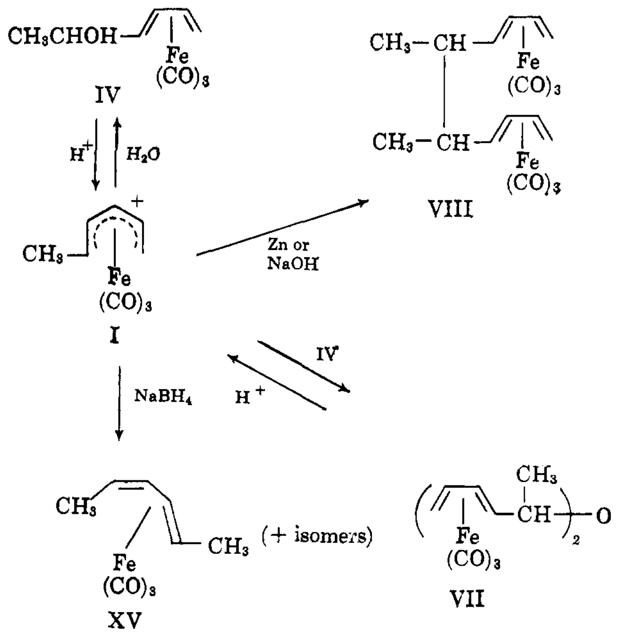


Fig. 1.—Proton nuclear magnetic resonance spectrum of *syn*-1-methylpentadienyliron tricarbonyl fluoroborate, peak positions are given in τ-units.

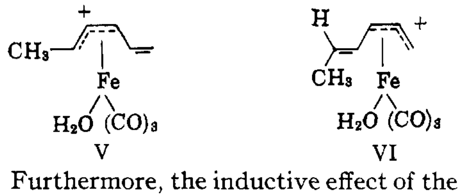
The chemical shifts of the various protons are closely related to those of the comparable protons in the parent cation and the *syn-syn*-dimethyl derivative. The absence of absorption in the region of 5.15 τ eliminates a cissoid structure having an *anti*-methyl group.[3] Further circumstantial evidence for the geometrical inversion which occurs in the formation of the cation from the alcohol complex II is seen in the reaction of I with water .

As with the parent cation and its 1,5-dimethyl derivative, salts of the cation I are soluble in water but very quickly hydrolyze to give an alcohol complex. In the present instance the cation gives a single new alcohol complex, isomeric with II, in yields greater than 90%. As indicated in the foregoing scheme the new alcohol complex is found to be *trans*-3,5-hexadien-2-ol-iron tricarbonyl (IV). Decomposition of IV with ferric chloride liberates 3,5-hexadien-2-ol which has been characterized by reduction to 2-hexanol. The *trans* configuration of the diene ligand in the complex IV is confirmed by the n.m.r. spectrum.



Now, since the two double bonds in a diene–iron tricarbonyl complex must be cissoid, the carbon atoms 3 and 6 in IV are *cis* with respect to the 4,5 bond. These particular atoms had the opposite configuration in the alcohol complex II and this again points to a geometrical inversion occurring in the formation of I from II.

An interesting feature of this reaction with water is the fact that it leads to the formation of just one of the two possible diastereoisomers of IV and, furthermore, to the exclusion of the isomeric complex II. The mechanism of hydrolysis of the dienyliron tricarbonyl cations, proposed in the previous paper,[1] would seem to allow a reasonable explanation for this result. Of the two intermediates V and VI, which would be involved in the formation of complexes II and IV, respectively, the latter might be expected to be the more stable for several reasons. The postulated intermediate VI contains the most substituted olefin and the least sterically crowded hydrated-π-allyliron tricarbonyl cation. Furthermore, the inductive effect of the methyl group might well be an unfavorable factor in a complex such as V for it would lead to a decrease in bonding *via* back donation from iron to the allyl system when compared to the system VI. The mechanism also allows one to predict that the configuration about C-2 and C-3 in the two enantiomorphic forms of IV will be R.R. and S.S. rather than S.R. and R.S. as would occur in the other diastereoisomer which, it is proposed, is not produced in this reaction.[4]



The cation I reacts with methanol and ethanol to give the related methyl and ethyl ethers of the alcohol complex IV. An ether complex VII is also formed upon reaction of I with the alcohol complex IV. The n.m.r. spectra indicate that a *trans* configuration about the C-3–C-4 bond exists in each of these ethers.[5] These

---

(3) See reference 7 of the preceding paper, Part II, J. E. Mahler and R. Pettit, *ibid.*, **85**, 3955 (1963).

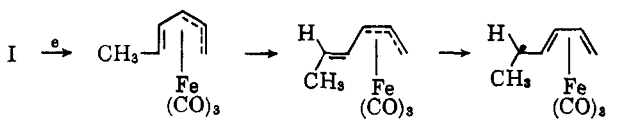
(4) For the purpose of assigning configurations to an unsymmetrical diene–iron tricarbonyl complex it is assumed that each carbon of the diene ligand is bonded to iron.

(5) The proton attached to the substituted terminal carbon atom of the diene ligand absorbs at 9.15 τ, which is characteristic of *anti* protons.

complexes also regenerate the cation I upon treatment with strong acids.

A particularly interesting reaction of the cation is seen upon treatment of salts of I with zinc. The crude product of this reaction is found to be a mixture consisting predominantly of two isomeric compounds. These substances, which appear to be present in approximately equal amounts, are shown to be diastereoisomers of 5,6-dimethyl-1,3,7,9-decatetraenediironhexacarbonyl (VIII). Quantitative separation of the crude reaction product has not proved possible; however, 80% of the mixture has been accounted for in terms of the two separated isomers and the infrared spectrum of the remaining material suggests that it consists largely of these same two compounds. The two isomers, hereafter referred to as A and B, possess practically identical infrared and n.m.r. spectra, though they differ by 20° in their melting points and show a pronounced mixture melting point depression. The free hydrocarbon ligands are obtained upon reaction of the complexes with ferric or ceric salts; oxidation with potassium permanganate of the hydrocarbon liberated from the higher melting isomer A produces *meso*-2,3-dimethylsuccinic acid, while compound B gives *racemic*-2,3-dimethylsuccinic acid in the same manner. The n.m.r. spectra of the free hydrocarbon ligands display olefinic-saturated protons in the ratio of 5:4 and the infrared spectra indicate the presence of both terminal vinyl groups and *trans*-substituted double bonds. These data all support the skeletal structure VIII for the two isomers.

The compounds A and B presumably arise through the dimerization of 1-methylpentadienyliron tricarbonyl free radicals. The preponderant formation of only two products is noteworthy, for literally scores of different compounds could conceivably arise through the random coupling of the various free radicals which can be written following addition of an electron to the cation I. From the data discussed before it would appear that the reaction proceeds almost entirely through dimerization of the radical X which could reasonably be produced in the following manner.

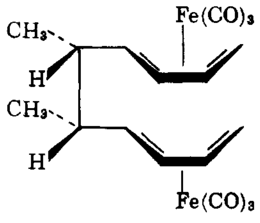


IXa IXb X

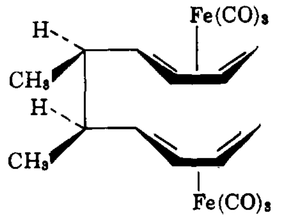
In the intermediate product IXa, formed following the addition of an electron to I, the double bond is not expected to be coordinated to the iron atom, else the effective atomic number of iron would exceed that of krypton; free rotation about the 3,4 single bond to give the structure IXb and thence X is, therefore, possible. A similar path leading to a structure having the unpaired electron on the terminal methylene carbon would be less likely because of similar steric and electronic effects noted before in analogous cationic intermediates V and VI.

This mechanism would serve to explain the observed skeletal structures of the two dimeric complexes. However, the radical species X together with its enantiomer may hypothetically couple to give rise to six different dimeric products having the skeletal structure shown by formula VIII; two will be *meso* forms and four will be *racemic* materials. The two *meso* forms together with one of the *racemic* compounds would give rise to *meso*-2,3-dimethylsuccinic acid upon oxidation, while the remaining three *racemic* compounds would give rise to *racemic*-2,3-dimethylsuccinic acid.

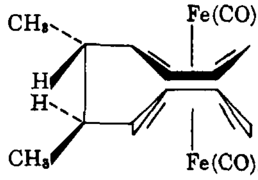
If, however, the reasonable assumption is made that the methyl group and the dieneiron tricarbonyl group are fixed *trans* about the C-1–C-2 bond in X (and in its enantiomer) and, furthermore, that the radicals combine with the bulky iron tricarbonyl groups opposed to each other, then only two dimeric products would be expected. Not only does this then account for the observed number of isomers, but it allows a prediction to be made as to the stereochemistry of A and B. For example, compound A is expected to be the *meso* structure XI rather than XII; similarly, compound B will be a racemate, one enantiomer of which will have structure XIII.



XI



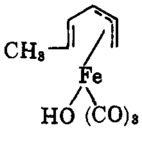
XII



XIII

A curious reaction ensues upon treatment of the cation I with potassium hydroxide. When conducted in a methanol–acetone solvent mixture, this reaction yields, as the major organometallic product, the same mixture of dimeric hydrocarbon iron tricarbonyls as produced in the foregoing reaction of I with zinc. Lesser amounts of the alcohol complex IV and its corresponding methyl ether, together with considerable amounts of iron hydroxide, are also obtained. The amount of dimeric product accounts for 30% of the salt employed. When the salt of I is added to sodium hydroxide in water, then the alcohol IV is the main product with only trace amounts of the dimer being formed.

One reasonable explanation for the formation of these dimeric complexes would involve attack of hydroxide ion at the iron nucleus of the cation I, thereby producing the neutral species XIV. The complex XIV could then undergo decomposition leading eventually to iron oxides, but in this oxidation process, electrons are transferred to further molecules of the cation I, thereby producing radicals which dimerize in the manner described earlier.



XIV

Further investigation has shown that the same type of reaction is found in the reaction of the cycloheptadienyliron tricarbonyl cation with sodium hydroxide. In this case the competing reaction leading to an alcohol complex is minimized and 60% of the cation is now converted to bis(cycloheptadienyl)diiron hexacarbonyl. The stereochemistry of the single dimeric product which is formed in this case has not been established.

These reactions with base appear to have an analogy in an earlier observation reported by Munro and Pauson[6]; these workers found that treatment of tropyliumchromium tricarbonyl salts with several nucleophiles

---

(6) J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 3479 (1961).

led to the formation of chromium tricarbonyl complexes of bis(cycloheptatrienyl). Part of the chromium was also oxidized in these reactions.

Treatment of the fluoroborate salt of the cation I with sodium borohydride gives a mixture of four isomeric hexadiene–iron tricarbonyl complexes. Vapor phase chromatography of the hydrocarbons liberated upon treatment of the mixture with ceric salts indicates that these complexes are present in the mixture in the ratio of 57:28:13:2. Hydrogenation of the mixture of hydrocarbons gives *n*-hexane.

The full characterization of this mixture of complexes has not been established. However, the n.m.r. spectrum shows a strong absorption (doublet) at 8.93 τ, indicative of a methyl group in the terminal *anti* position of a diene–iron tricarbonyl complex. This must arise from the presence of *cis-trans*-2,4-hexadieneiron tricarbonyl in the mixture; the relative areas suggest that it is the major component. The absence of a quartet in the region 9.6–9.8 τ also indicates that *trans*-1,3-hexadieneiron tricarbonyl is, at most, a very minor component. The other compounds present are, therefore, most likely to be iron tricarbonyl derivatives of *cis*-1,3- and *trans-trans*-2,4-hexadiene. In any event the reaction with sodium borohydride is clearly not as selective as the other reactions discussed before.

Treatment of the crude mixture of hexadiene–iron tricarbonyl complexes with triphenylmethyl fluoroborate regenerates the complex cation I in yields of 36%; this confirms that the reaction of I with sodium borohydride leads, to a significant extent, to products in which geometrical inversion of the ligand does not occur.

The reason why sodium borohydride appears to attack I predominantly at the C-5 position of the ligand is not clear; perhaps it simply involves direct attack of the nucleophile on the least hindered position of the ligand.

Experimental

Preparation of *trans-trans*-2,4-Hexadien-1-ol-iron Tricarbonyl. A. Reaction of Iron Pentacarbonyl with *trans-trans*-2,4-Hexadien-1-ol.—A mixture of 67.5 g. of *trans-trans*-2,4-hexadien-1-ol and 160 g. of iron pentacarbonyl was refluxed under nitrogen for 96 hr. The volatile materials were removed under reduced pressure; distillation of the residue yielded 27.0 g. of *trans-trans*-3,5-hexadien-1-ol-iron tricarbonyl, b.p. 96° (0.3 mm.), n^{31}D 1.5850. The complex became solid when cooled and crystallization from petroleum ether afforded yellow needles, m.p. 37°.

Anal. Calcd. for $C_9H_{10}O_4Fe$: C, 45.41; H, 4.23. Found: C, 45.67; H, 4.15.

An infrared spectrum showed bands at 3340 cm.$^{-1}$ (OH) and at 2049, 1982, 1975 cm.$^{-1}$ (C≡O).

B. Reduction of *trans-trans*-2,4-Hexadienaliron Tricarbonyl.—Sodium borohydride (6.0 g.) was added in small portions to a stirred solution of 102.0 g. of *trans-trans*-2,4-hexadienaliron tricarbonyl in 500 ml. of methanol. The reaction mixture was maintained at 25–35° throughout the addition. After the final addition, stirring was maintained for 30 min.; then the mixture was added to 500 ml. of water and extracted with three 250-ml. portions of ether. The combined ether extracts were washed with water, then dried over magnesium sulfate. Removal of the solvent left 97.0 g. of crude alcohol complex. Recrystallization of this material gave *trans-trans*-2,4-hexadien-1-ol-iron tricarbonyl, identical with that prepared in section A.

For purposes of making salts of I, the crude product, without further purification, is satisfactory (see below).

Preparation of Salts of *syn*-1-Methylpentadienyliron Tricarbonyl. A Perchlorate Salt.—A solution of 3.0 g. of 70% perchloric acid in acetic anhydride (prepared by adding the acid to 10 ml. of acetic anhydride at 0°) was added slowly to a stirred solution of 5.0 g. of *trans-trans*-2,4-hexadien-1-ol-iron tricarbonyl in 20 ml. of acetic anhydride at 0°. During the course of the addition, yellow crystals separated. The reaction mixture was stirred for 30 min., then poured into excess dry ether. Filtration yielded 6.3 g. of *syn*-1-methylpentadienyliron tricarbonyl perchlorate. The salt crystallizes from nitromethane in yellow needles which explode violently when heated.

Anal. Calcd. for $C_9H_9O_7ClFe$: C, 33.73; H, 2.83; Cl, 11.07. Found: C, 33.49; H, 2.87; Cl, 10.89.

An infrared spectrum taken in nitromethane showed absorptions at 2120 and 2072 cm.$^{-1}$ (C≡O).

B. Fluoroborate Salt.—The crude alcohol complex, prepared by the reduction of 102.0 g. of *trans-trans*-2,4-hexadienaliron tricarbonyl with sodium borohydride, was dissolved in 125 ml. of acetic anhydride. This mixture was then added slowly to a stirred solution of 75.4 g. of aqueous 50% fluoroboric acid dissolved in 150 ml. of acetic anhydride (caution). The temperature was maintained at 5–10° throughout the addition. After 30 min. following the addition the mixture was poured into 400 ml. of anhydrous ether. The yellow precipitate was washed thoroughly with anhydrous ether, then dried in air. The yield of fluoroborate salt was 115 g. The salt crystallized in yellow prisms from nitromethane, dec. pt. 195°.

Reactions of the *syn*-1-Methylpentadienyliron Tricarbonyl Cation. A. With Water.—*syn*-1-Methylpentadienyliron tricarbonyl perchlorate (5.0 g.) was added to 100 ml. of water. The initial clear solution rapidly turned milky due to the appearance of a finely divided crystalline precipitate. After stirring for 30 min., the reaction mixture was extracted with pentane. The pentane extracts were washed with water and then dried over magnesium sulfate. Solvent removal left 3.5 g. of *trans*-3,5-hexadien-2-ol-iron tricarbonyl. Crystallization from petroleum ether afforded yellow needles, m.p. 65°.

Anal. Calcd. for $C_9H_{10}O_4Fe$: C, 45.41; H, 4.23; mol. wt., 238. Found: C, 45.40; H, 4.57; mol. wt., 242.

An infrared spectrum in carbon tetrachloride showed bands at 3350 cm.$^{-1}$ (OH) and 2053, 1988, and 1977 cm.$^{-1}$ (C≡O).

The alcohol complex was degraded with ferric chloride and the liberated dienol was hydrogenated (platinum oxide in acetic acid) to give the saturated alcohol. The saturated alcohol was shown, by comparison of its infrared spectrum to that of an authentic sample, to be 2-hexanol.

The saturated alcohol was oxidized with chromic acid to 2-hexanone which was converted to its 2,4-dinitrophenylhydrazone derivative, m.p. 106°; mixture with an authentic sample gave no depression of the melting point.

B. With Methyl Alcohol.—*syn*-1-Methylpentadienyliron tricarbonyl fluoroborate (5.0 g.) was dissolved in 25 ml. of methyl alcohol. The solution was stirred for 30 min., poured into excess water, and extracted several times with light petroleum. The combined extracts were washed with water and dried over magnesium sulfate. Distillation, after solvent removal, afforded 3.52 g. of *trans*-2-methoxy-3,5-hexadieneiron tricarbonyl, b.p. 58° (0.1 mm.), n^{29}D 1.5504. Crystallization from light petroleum yielded yellow crystals, m.p. 39°.

Anal. Calcd. for $C_{10}H_{12}O_4Fe$: C, 47.65; H, 4.80. Found: C, 47.53; H, 4.82.

An infrared spectrum taken in carbon tetrachloride showed bands at 2048, 1985, and 1971 cm.$^{-1}$ (C≡O) and at 1083, 1095, and 1110 cm.$^{-1}$.

C. With Sodium and Potassium Hydroxides.—*syn*-1-Methylpentadienyliron tricarbonyl fluoroborate (13.0 g.) was added to a solution of 3.0 g. of potassium hydroxide, 25 ml. of methanol, and 200 ml. of acetone at −30°. The solution was stirred at this temperature for 25 min., warmed to 10°, poured into excess water, and extracted three times with ether. The combined extracts were washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a viscous oil which was chromatographed over alumina. The chromatography afforded 2.64 g. of 5,6-dimethyldeca-1,3,7,9-tetraenediiron hexacarbonyl (eluted with light petroleum), m.p. 108–126°. This mixture was then separated by crystallization from light petroleum into the same two diastereoisomers (A and B) obtained from the reaction of 1-methylpentadienyliron tricarbonyl fluoroborate with zinc (see below). The melting points, mixture melting points, and n.m.r. spectra of the mixture or of its two components were identical with those of the isomers obtained from the zinc reaction.

In addition, the chromatography mentioned before afforded 0.90 g. of the methyl ether of 3,5-hexadien-2-ol-iron tricarbonyl (eluted with benzene) and 1.79 g. of 3,5-hexadien-2-ol-iron tricarbonyl (eluted with 5% ethanol–benzene).

In another reaction, 2.2 g. of sodium hydroxide in 20 ml. of water and 200 ml. of acetone were added slowly to a cold (0°) solution of 15.4 g. of fluoroborate salt in 400 ml. of acetone. This mixture was worked up in the manner described in section B. Chromatography of the product afforded 0.8 g. of dimeric complex and 9.0 g. of *trans*-3,5-hexadien-2-ol-iron tricarbonyl.

D. With *trans*-3,5-Hexadien-2-ol-iron Tricarbonyl.—A solution of 1.2 g. of *trans*-3,5-hexadien-2-ol-iron tricarbonyl in 5 ml. of nitromethane was treated with 2.3 g. of 1-methylpentadienyliron tricarbonyl fluoroborate. The solution was cooled in an ice bath for 1 hr.; the crystalline solid that formed was then filtered to yield 1.6 g. of di-2-(*trans*-3,5-hexadieneiron tricarbonyl)ether. The complex crystallizes from pentane as small yellow plates, m.p. 118–120°.

Anal. Calcd. for $C_{18}H_{18}O_7Fe$: C, 47.19; H, 3.96. Found: C, 47.49; H, 3.90.

E. With Sodium Borohydride.—Sodium borohydride (3.0 g.) was added over a 10-min. period to a stirred suspension of 22.0 g. of *syn*-1-methylpentadienyliron tricarbonyl fluoroborate in 300 ml. of dry tetrahydrofuran at −30°. After the addition, the temperature of the reaction mixture was maintained at −30° for 20 min. The reaction mixture was then warmed to 10°, poured into excess water, and extracted several times with light petroleum. The combined extracts were washed with water and dried over magnesium sulfate. The solvent was removed and the residual oil was distilled to give 8.4 g. of a mixture of hexadiene–iron tricarbonyls, b.p. 47–49° (0.35 mm.), $n^{30}\text{D}$ 1.5620.

Anal. Calcd. for $C_9H_{10}O_3Fe$: C, 48.68; H, 4.54. Found: C, 48.83; H, 4.58.

An infrared spectrum in carbon tetrachloride showed absorption at 1972 (broad) and 2042 cm.$^{-1}$ ($C\equiv O$).

A solution of 0.52 g. of the mixture of hexadiene–iron tricarbonyls in 2 ml. of nitromethane was added slowly to a stirred solution of 0.93 g. of triphenylmethyl fluoroborate in 6 ml. of nitromethane. The solution was warmed to 50° for 10 min., then poured into excess dry ether to precipitate the salt. The suspension was stirred for 20 min. to decompose excess triphenylmethyl fluoroborate, then filtered to yield 0.25 g. (36%) of *syn*-1-methylpentadienyliron tricarbonyl fluoroborate; an infrared spectrum taken as a Nujol mull was identical with that of an authentic sample.

In a separate experiment, using dichloromethane as solvent, the reaction mixture was poured into pentane. The suspension in pentane was filtered and the solvent removed from the filtrate. Crystallization of the residual solid from ethanol yielded triphenylmethane, m.p. 94–95.5°; admixture with an authentic sample gave no depression of the melting point.

Reaction of *trans-trans*-2,4-Hexadien-1-ol-iron Tricarbonyl with Triphenylmethyl Fluoroborate.—Triphenylmethyl fluoroborate (1.92 g.) in 10 ml. of dichloromethane was added to 1.13 g. of *trans-trans*-2,4-hexadien-1-ol-iron tricarbonyl in 2 ml. of dichloromethane at ambient temperature. Yellow crystals formed immediately and after cooling to 0° for 10 min., filtration yielded 1.29 g. of *syn*-1-methylpentadienyliron tricarbonyl fluoroborate. An infrared spectrum taken in a Nujol mull was identical with that of an authentic sample of the salt.

Removal of the solvent from the filtrate from above, followed by recrystallization of the solid from ether, gave 0.70 g. of triphenylcarbinol, m.p. 162–163°; a mixture melting point with an authentic sample gave no depression.

Attempts to extract the hydroxyl group from *trans-trans*-2,4-hexadien-1-ol-iron tricarbonyl by treating it with tropylium perchlorate in dichloromethane failed. Variations of molar quantities, reaction time, and temperature all resulted in no reaction.

Degradation of *trans-trans*-2,4-Hexadien-1-ol-iron Tricarbonyl.—A solution of 5.0 g. of *trans-trans*-2,4-hexadien-1-ol-iron tricarbonyl in 20 ml. of ethanol was added dropwise to a stirred solution of 16.0 g. of ferric chloride hexahydrate in 50 ml. of ethanol at room temperature. The reaction mixture was stirred for 2 hr., poured into excess water, and extracted with ether. The ether extracts were washed with 5% sodium carbonate and water and were dried over sodium sulfate. Distillation, after solvent removal, afforded *trans-trans*-2,4-hexadien-1-ol, b.p. 88° (30 mm.). An infrared spectrum of this alcohol was identical with that of an authentic sample.

Zinc Reduction of *syn*-1-Methylpentadienyliron Tricarbonyl Fluoroborate.—A suspension of 84 g. of *syn*-1-methylpentadienyliron tricarbonyl fluoroborate and 89 g. of zinc dust in 500 ml. of freshly distilled tetrahydrofuran was stirred at ambient temperature (*ca.* 25°) for 72 hr. The slurry was filtered through Celite and the solvent removed under reduced pressure. The residual solid was treated with 200 ml. of boiling petroleum ether and quickly filtered through Celite. The filtrate, upon cooling to −78°, yielded 43.0 g. (71%) of yellow crystalline solid, m.p. 105–120°. Successive recrystallization from petroleum ether of 43.0 g. of the crude product yielded 18.0 g. of one isomer, m.p. 123–126° (described in the text as "B") and 15.0 g. of the other isomer, m.p. 143–146° (described in the text as "A"). A mixture of these two isomers gave a melting point of 108–129°.

Anal. Calcd. for $C_{18}H_{18}O_6Fe_2$: C, 48.91; H, 4.10. Found (for "A"): C, 48.96; H, 3.96. Found (for "B"): C, 48.88; H, 3.98. The proton n.m.r. spectrum of A in carbon tetrachloride solution showed absorption at 4.81, 8.24, 8.89, and 9.74 τ, while B showed absorption at 4.83, 8.28, 8.92, and 9.77 τ; the relative areas of these bands in each case was 2:1:5:1. The infrared spectrum of compounds A and "B," obtained in carbon tetrachloride solution, exhibited bands at 1971, 1983, and 2046 cm.$^{-1}$ ($C\equiv O$).

A solution of 0.75 g. of the unsaturated hydrocarbons (obtained by degrading a mixture of the complexes A and B) in 40 ml. of glacial acetic acid was hydrogenated (platinum oxide) to yield 0.44 g. of 5,6-dimethyldecane, b.p. 97° (30 mm.); the infrared and n.m.r. spectra of the saturated hydrocarbons were identical with those of an authentic sample of 5,6-dimethyldecane.[7]

A solution containing 160.0 g. of ceric ammonium nitrate, 525 ml. of ethanol, and 175 ml. of water was added to a stirred solution of 19.0 g. of complex B in 150 ml. of acetone at ambient temperature. The mixture was stirred an additional 20 min. and then extracted with ether. The combined ether extracts were washed with saturated brine and dried over magnesium sulfate. Removal of the solvent and distillation of the residue afforded 6.22 g. (89%) of 5,6-dimethyldecatetraene, b.p. 39° (0.5 mm.), $n^{25}\text{D}$ 1.5033.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.83, H, 11.18. Found: C, 88.65; H, 11.09.

An infrared spectrum (neat) of this compound exhibited absorption at 895, 1001, and 1800 cm.$^{-1}$ ($-CH=CH_2$); 949 cm.$^{-1}$ (*trans* $C=C$); 1605 and 1651 cm.$^{-1}$ (conj. diene).

An n.m.r. spectrum (neat) showed complex multiplets centered at 4.39 τ (olefinic protons) and at 7.82 τ (methine protons) and a doublet at 9.01 τ (methyl protons) with relative areas 5:1:3, respectively.

Powdered potassium permanganate (8.84 g.) was added slowly to a stirred mixture of 1.0 g. of the hydrocarbon derived from complex B and 100 ml. of water. The mixture was stirred at ambient temperature for 20 hr., then filtered through Celite, and the filtrate was acidified with 6 *M* sulfuric acid. The organic acid was extracted six times with ether and the combined ether extracts were dried over magnesium sulfate. Evaporation of the solvent afforded 100 mg. of *dl*-2,3-dimethylsuccinic acid which was then recrystallized from 6 *M* hydrochloric acid, m.p. 122–124° (lit. 122–123°).

Treatment of 20 g. of complex A with ceric ammonium nitrate in the manner described for complex B afforded 5,6-dimethyldecatetraene (5.0 g.), b.p. 32° (0.38 mm.), $n^{25}\text{D}$ 1.5026.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.71; H, 11.24.

An infrared spectrum (neat) of this unsaturated hydrocarbon exhibited absorption at 895, 1001, and 1800 cm.$^{-1}$ ($-CH=CH_2$); 948 cm.$^{-1}$ (*trans* $C=C$); 1604 and 1652 cm.$^{-1}$ (conj. diene).

An n.m.r. spectrum (neat) of this unsaturated hydrocarbon showed complex multiplets centered at 4.39 τ (olefinic protons) and at 7.92 τ (methine protons) and a doublet at 9.02 τ (methyl protons) with relative areas 5:1:3, respectively.

Oxidation of a 1.0-g. sample of this unsaturated hydrocarbon, in the manner described previously, afforded 100 mg. of crude acidic material. Recrystallization from 6 *M* hydrochloric acid followed by vacuum sublimation yielded *meso*-2,3-dimethylsuccinic acid, m.p. 207–208°; admixture with an authentic sample showed no depression.

Reaction of Cycloheptadienyliron Tricarbonyl Fluoroborate with Sodium Hydroxide.—Cycloheptadienyliron tricarbonyl fluoroborate[8] (6.4 g.) was added slowly to a heterogeneous mixture of 20 ml. of 50% sodium hydroxide, 60 ml. of water, 220 ml. of acetone, 50 ml. of ether, and 50 ml. of pentane at −35°. The reaction mixture was stirred for 10 min. at −35°, warmed rapidly to 0°, and the organic layer was separated. The aqueous solution was extracted three times with ether. The combined extracts were washed with water and dried over magnesium sulfate. Removal of the solvent afforded 2.8 g. of solid bis(cycloheptadienyl)diiron hexacarbonyl. Recrystallization from light petroleum afforded the complex as yellow crystals, m.p. 176°.

Anal. Calcd. for $C_{20}H_{18}O_6Fe_2$: C, 51.54; H, 3.89; mol. wt., 465. Found: C, 51.29; H, 3.74; mol. wt., 412.

An infrared spectrum taken in carbon tetrachloride exhibited absorption at 2046, 2041, and 1977 cm.$^{-1}$ ($C\equiv O$).

Acknowledgments.—We wish to thank the National Science Foundation, the Robert A. Welch Foundation, and the Alfred P. Sloan Foundation for financial support. We also thank Antara Chemicals for a generous gift of iron carbonyl.

---

(7) 5,6-Dimethyldecane was prepared by a Wurtz reaction with 2-bromohexane.

(8) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).