The Isolation, Structure and Properties of a New π-Diene-Iron Tricarbonyl Complex Formed from Methyl Linolate and Iron Pentacarbonyl

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A π-diene-iron tricarbonyl complex, the formation of which in the process of the hydrogenation of cotton seed oil with the iron pentacarbonyl catalyst was reported on in a previous paper,[1] has now been prepared for the first time and isolated by the following procedure: A mixture of fatty acid methyl ester of dehydrated castor oil (30 g.) and iron pentacarbonyl (13.7 ml.) was heated repeatedly under nitrogen at 180°C in a stainless-steel bomb until the evolution of carbon monoxide ceased. The ether solution of the reaction mixture was then washed with aqueous hydrochloric acid (1 : 1) and with water. After the solvent had been removed, a few drops of low-boiling materials were distilled off at 0.1 mmHg below 205°C, the temperature of the bath. The remaining liquid was distilled in a magnetic-stirred pot-type molecular distillation still; as a last fraction, about 8 g. of a yellow-orange oil was obtained. B. p. 79~90°C/10^{-4} mmHg; d_4^{28} 1.092; n_D^{26} 1.5158; mol. wt. (ebullioscopic in MEK), 414; Found: C, 62.2; H, 8.1; Fe, 12.8. Calcd. for $C_{22}H_{34}O_5Fe$: C, 60.8; H, 7.9; Fe, 12.9%.

An attempt to isolate the compound by chromatography over alumina (Woelm, grade II.) with petroleum benzine was unsuccessful.

The infrared spectrum taken in carbon disulfide shows characteristic M–C≡O bands at 2045 and 1975 cm^{-1} ($E_{cm}^{\%}=93$ at $I/I_0=0.5$), and these bands agree closely with those of cyclooctadiene-iron tricarbonyl.[2]

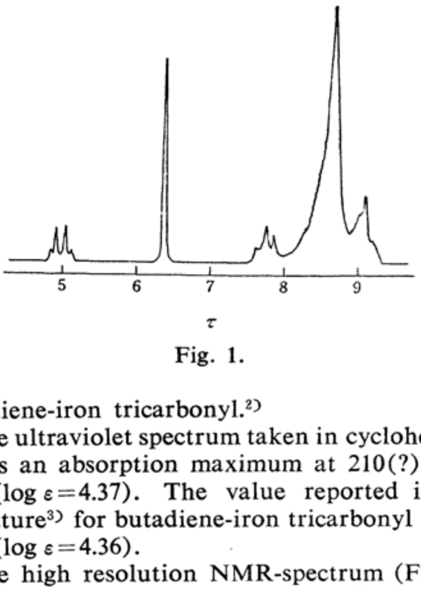

Fig. 1.

The ultraviolet spectrum taken in cyclohexane shows an absorption maximum at 210(?)~220 mμ ($\log \varepsilon=4.37$). The value reported in the literature[3] for butadiene-iron tricarbonyl is 211 mμ ($\log \varepsilon=4.36$).

The high resolution NMR-spectrum (Fig. 1) taken in carbon tetrachloride at 60 Mc. indicates the following signals (range in τ-value, relative intensity, structure and/or assignment): 4.8~5.2, 2, double-triplet, coordinated olefinic protons; 6.3~6.5, 3, $-OCH_3$; 7.5~7.9, 2, $-CH_2-CO-$; 7.9~9.4, 27, two overlapped, unsymmetrical bands, aliphatic protons. By analogy from the spectra of the iron tricarbonyl complexes of butadiene, 1,3-cyclohexadiene, and

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[1] A. Misono, I. Ogata and F. Funami, *J. Japan Oil Chem. Soc.* (*Yukagaku*), **13**, 21 (1964).

[2] K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

[3] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, **1958**, 643.

1, 3-cycloheptadiene,⁽4⁾ the lowest-field band may be assigned to the "central" protons of a coordinated conjugate system.

Ligand-exchange reaction with triphenylphosphine in liquid paraffin in a tube at 150°C for 24 hr. afforded yellow crystals, the infrared spectrum of which is identical with that of bis(triphenylphosphine)-iron tricarbonyl.⁽5⁾ From the infrared spectrum and from the gas-liquid chromatography, the remaining liquid proved mainly to be one of the stereoisomers of methyl-C_{18}-conjugated-diene-carboxylate.

These results indicate that this compound is the iron tricarbonyl complex of methyl-C_{18}-conjugated-diene-carboxylate formed from methyl linolate by isomerization reaction.

The complex is reasonably stable in the condensed state, but it is readily decomposed in solution, even under nitrogen in a dark, cold place, and gives brown or black precipitates. When treated above its decomposition temperature (ca. 225°C), a mixture of this complex and diene-carboxylic acid ester polymerized mainly to the dimer of the acid ester. By hydrocracking at 200°C (100 atm. in a stainless-steel bomb), the complex was converted mainly to methyl stearate.

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4) M. L. H. Green, L. Pratt and G. Wilkinson, ibid., **1959**, 3753; R. Burton, L. Pratt and G. Wilkinson, ibid., **1961**, 594.

5) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).