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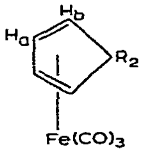
SHORT COMMUNICATION

Spiro[4.4]nona-1,3-dieneiron tricarbonyl

The appearance of a paper by Kochhar and Pettit[1] describing their elegant work on the preparation and behaviour of cyclopentadieneiron tricarbonyl (Ia) prompts us to report our isolation[2] of the title compound (Ib). Compound (Ia) had long been assumed to be an intermediate in the formation of the binuclear product (IIa) from cyclopentadiene and iron pentacarbonyl. The ease of this transformation has now been established[1]. Some years ago[3] we attempted to block such transformation by using spiro[4.4]nona-1,3-diene. But in place of the expected complex (Ib), iron pentacarbonyl only yielded the binuclear complex (IIb) whose formation involves a rearrangement of the carbon skeleton. We now find that nonacarbonyldiiron reacts smoothly with the spirodiene in refluxing benzene to give the tricarbonylspirodiene compound (Ib). Like other tricarbonyldiene complexes of iron this shows two strong infrared maxima in the carbonyl stretching region near 2050 and 1950 cm^{-1}. Its structure is confirmed by its NMR spectrum: The A_2B_2 system of the unsaturated ring gives rise to overlapping doublets which appear as triplets centred at $\tau = 4.58$ (H_a) and 7.05 (H_b). The four methylene groups are all in different environments and give rise to a complex group of peaks between $\tau = 8$ and 9. Above 140° the spiro compound (Ib) decomposes to give the previously described[3] tetrahydroindenyl complex (IIb), albeit in low yield; optimum conditions for this conversion have not been established.



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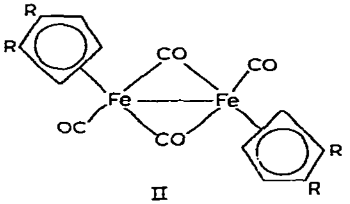

II

(a) $R = H$; (b) $R_2 = (CH_2)_4$

Experimental

A mixture of nonacarbonyldiiron (1.5 g), spiro[4.4]nona-1,3-diene[4] (0.5 g) and benzene (25 ml) was refluxed under nitrogen for 1.5 h. The filtered solution was evaporated *in vacuo* and distilled to give tricarbonylspiro[4.4]nona-1,3-dieneiron (Ib) (0.32 g, 31 %), a brownish-yellow oil, distilling from a bath at 100°/2 mm. (Found: C, 55.2; H, 4.9; O, 18.4. $C_{12}H_{12}FeO_3$ calcd.: C, 55.5; H, 4.6; O, 18.4%.)

A sample of this product was heated to 145° under nitrogen. Chromatography of the residue on alumina gave unchanged starting material and a small amount of the binuclear complex (IIb), identified by infrared comparison with an authentic sample[3]. Attempts to effect this pyrolysis in refluxing chlorobenzene, ethylbenzene or di-n-butyl ether were unsuccessful.

When a mixture of the tricarbonyl (Ib) (1.1 g) and triphenylphosphine (1.8 g) in benzene (400 ml) was irradiated for 24 h with a 500 W medium-pressure mercury vapour lamp, one carbonyl group was replaced by the phosphine. Dicarbonyltriphenylphosphinespiro[4.4]nona-1,3-dieneiron was isolated, after chromatography, as golden yellow crystals, m.p. 153°. Much tricarbonyl (Ib) was recovered. The low yield and difficulty in recrystallising the product prevented complete characterisation. The structure of this phosphine substituted complex follows by analogy with the behaviour of other diene complexes[5] and especially the appearance in its infrared spectrum of carbonyl stretching peaks at 1962 and 1900 cm^{-1}.

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