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NOTE

FORMATION AND REARRANGEMENTS OF IRON CARBONYL COMPLEXES OF SPIRO[2.4]HEPTA-4,6-DIENE

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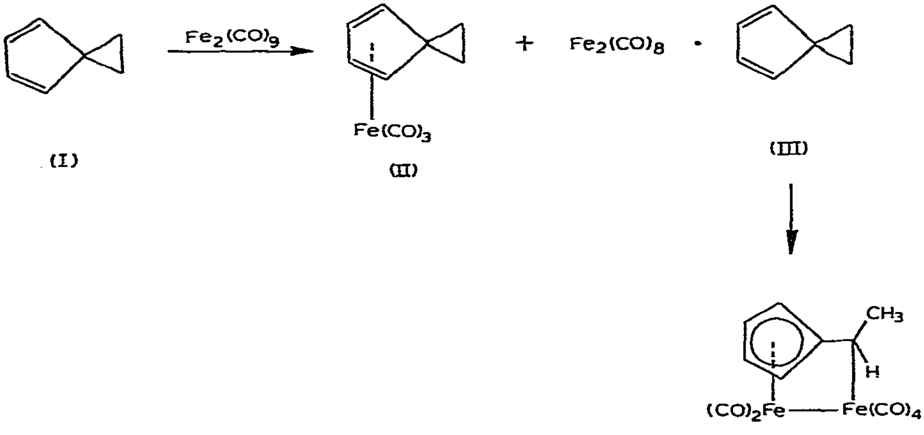
In 1958, Hallam and Pauson[1] reported that spiro[2.4]hepta-4,6-diene (I) and spiro[4.4]nona-1,3-diene formed only ring-opened, binuclear complexes upon reaction with iron pentacarbonyl at elevated temperatures. Recently, Grant and Pauson[2] obtained the tricarbonyl complex of the latter diene by reaction of the hydrocarbon with iron nonacarbonyl. We wish to report the isolation of the expected iron tricarbonyl complex (II) from diene (I) and, in addition, a second compound (III) which gradually rearranges to (6-methylfulvene)diiron hexacarbonyl (IV).



(I) (II) (III)

(IV)

EXPERIMENTAL

In a typical preparation of compounds (II) and (III), 4.0 g of spiro[2.4]hepta-4,6-diene[1] was added to a slurry of 20.0 g of $Fe_2(CO)_9$ and 200 ml of anhydrous ether. The reaction vessel was purged with nitrogen, fitted with a mercury bubbler and stirred for 16 h at room temperature. The mixture was filtered through Celite and the solvent removed on a rotary evaporator. The residue was taken up in 150 ml of hexane and allowed to stand at −20° for several hours. During this time the majority of the tricarbonyl compound (II) crystallized as bright yellow needles, m.p. 108–110°. (Found: C, 51.71; H, 3.52; O, 20.81. $C_{10}H_8FeO_3$ calcd.: C, 51.72; H, 3.47; O, 20.68%.)

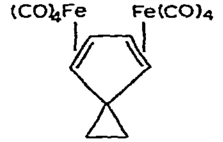
The mass spectrum of (II) exhibits the parent molecular ion at *m/e* 232 and peaks at *m/e* 204, 176, 148 and 92 corresponding to the successive losses of three CO ligands and finally the iron atom. The NMR spectrum of compound (II) (obtained in deuteriobenzene) exhibited triplets at τ 8.53, 6.82, 5.95 and 5.61, all with relative ratios of 1. The IR spectrum of (II) (CCl_4) exhibited $\nu(C\equiv O)$ at 1980 and 2030 cm^{-1}. Compound (III) was obtained from the hexane mother liquors upon further standing at $-20°$. Several subsequent crystallizations from hexane afforded deep red needles, m.p. 70° dec., whose IR spectrum (obtained in CCl_4) exhibited $\nu(C\equiv O)$ at 1985, 1995 and 2080 cm^{-1}. An NMR sample of (III), in deuteriobenzene solution, was prepared in a dry box under nitrogen; the spectrum exhibited triplets of relative area 1 at τ 8.68, 7.57, 6.05 and 5.78. The yields of compounds (II) and (III) were 3.9 and 2.0 g, respectively.

A sample of (III) was allowed to stand at room temperature until its IR spectrum indicated that it had been converted to (IV) (*ca.* 18 h). The fulvene complex (IV) was then purified by sublimation *in vacuo* (65° at 15 mm). The pure material had m.p. 90° dec. (Found: C, 42.65; H, 2.45. $C_{13}H_8Fe_2O_6$ calcd.: C, 41.98; H, 2.16%.)

Its IR spectrum (hexane) exhibited $\nu(C\equiv O)$ at 1950, 1980, 2000, 2010, 2030 and 2080 cm^{-1}. The fulvene complex (IV) exhibits the parent molecular ion at *m/e* 372 followed by major peaks at *m/e* 346, 318, 288, 260, 232, 204, 176, 148 and 92. The NMR spectrum of (IV) (obtained in deuteriobenzene) showed a doublet at τ 8.98, a quartet at 8.25 and multiplets at 7.25, 6.91 and 6.36; the relative ratios were 3/1/1/1/2, respectively.

RESULTS AND DISCUSSION

The IR, mass spectrum and NMR spectrum of the tricarbonyl complex (II) are fully in accord with its suggested structure. The instability of compound (III), the diiron octacarbonyl complex, has so far precluded analytical or mass spectral analysis and its structure remains hypothetical*. Its NMR spectrum closely resembles that of the tricarbonyl complex except that each set of signals in (III) appears at higher field than the corresponding set in (II). On the basis of the NMR and IR spectra and of the structure of the rearrangement product, we are tentatively assigning the structure shown below. Upon standing at room temperature overnight, compound (III) is converted cleanly to a second red crystalline compound whose analytical and spectral properties are in agreement[4] with its assignment as (6-methylfulvene)diiron hexacarbonyl. In view of the recent X-ray analysis of fulvenediiron hexacarbonyl, the 6-methyl derivative is probably best represented as structure (IV)[5].



The rearrangement of a vinylcyclopropane system to a diene complex under the influence of an iron carbonyl has been reported previously by Sarel *et al.*[6]. The

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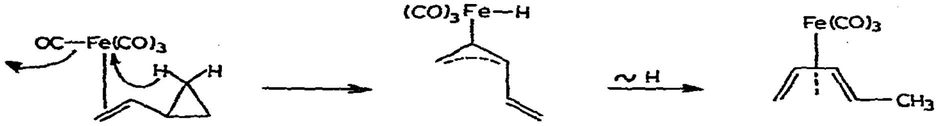
* See, however, ref. 3 for a comparison of related iron tetracarbonyl complexes.



mechanism which they proposed, involving the formation of an iron–carbon bond, is sterically impossible in the present case. We propose the alternative mechanism shown above, which draws analogy from other hydrogen transfer reactions among iron–carbonyl complexes[7,8,9].

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