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CHEMICAL AND ELECTROCHEMICAL HYDROGENATION OF CYCLOOCTATETRAENE TRICARBONYL IRON

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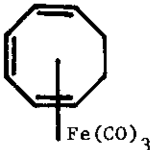
The direct reaction of iron carbonyl compounds with the mixture of isomers resulting from the reduction of cyclooctatetraene has been studied by several workers[1,2,3].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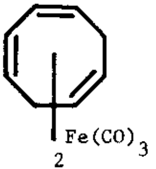
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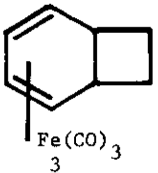
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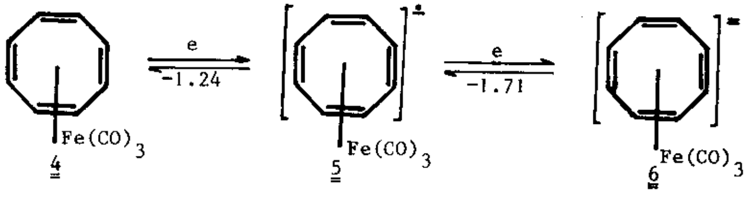
Of the two possible cyclooctatriene tricarbonyl iron 1 and 2, only 1 is formed, but 3 is also obtained under certain conditions. 1 has thus been prepared in 20 % yield by McFarlane, Pratt and Wilkinson[3], and in 56 % yield by Brookhart, Lippman and Reardon[4]. 1 can readily be converted to 3.

Another possible route to 1 and 2, the direct reduction of cyclooctatetraene tricarbonyl iron 4, had never been attempted. We report here the results of a chemical and electrochemical reduction of 4. A preliminary study by polarography and cyclic voltammetry (DMF, Hg electrode, $(CH_3)_4N^+BF_4^-$ 0.2 M) showed that 4 is reduced in two reversible 1 F stages ($E_{1/2}$ = - 1.24 and - 1.71 V E.C.S.). $E_{1/2}$ values of - 2 and - 2.5 have been found in diglyme[5]. The reduction leads to the radical anion 5 and to the dianion 6.



Reduction of cyclooctatetraene tricarbonyl iron by potassium.

Reaction of 4 in anhydrous THF with a slight excess of potassium, at room temperature and under inert atmosphere, affords a red brown solution. In the IR spectrum of this solution, the characteristic ν (CO) stretching frequencies of 4 are replaced by three very large bands in the range 1950-1850 cm^{-1}, showing that complete reduction of 4 has been achieved. Addition of water and extraction with ether gives an orange solution which is dried over $MgSO_4$. The orange filtrate is evaporated under vacuum and the orange-red oily residue is dissolved in the minimum amount of n-hexane. Chromatography on an alumina column, using n-hexane as the eluent, affords 1 and 4, each in 30 % yield. (1 was identified by its IR and NMR spectra). This result can be explained as follows : the reduction by potassium does not go beyond the first stage. In the solution, 5 is in equilibrium with small amounts of 6 and 4. The protonation takes place on 6 to give 1, which is accompanied by a dismutation leading to the same quantity of 4. The yield of the reaction is thus necessarily limited to 50 %.

$$\underline{\underline{4}} \rightleftharpoons \underline{\underline{5}} \rightleftharpoons \underline{\underline{6}} \longrightarrow \underline{\underline{1}}$$

This interpretation is confirmed by a study by cyclic voltammetry. The addition of H^+ ions has the following consequences : a) the second stage becomes irreversible even at high sweep rates ($100\ V.s^{-1}$), and the reduction potential becomes more positive. b) the first stage becomes irreversible only when the scan rate is smaller than $0.2\ V.s^{-1}$. This shows that the reaction of H^+ ions with the dianion is very rapid. The disappearance of the radical anion 5, which takes place through 6 is much slower, since the concentration of 6 in a solution of 5 is very small : the dismutation constant K of the radical anion is $K = [\underline{\underline{4}}][\underline{\underline{6}}] / [\underline{\underline{5}}]^2 = \exp[-(F/RT)(\Delta E_{1/2})] = 1.136 \times 10^{-8}$ so that $[\underline{\underline{6}}] \approx 10^{-4} \times [\underline{\underline{5}}]$.

Electrochemical reduction.

In the presence of a proton donor $[(CH_3)_3N, HBr]$, 4 shows a 2 F wave ($E_{1/2} = -1.13$ V E.C.S.). After electrolysis of the solution at − 1.3 V, an orange solution is obtained, which, treated as above, gives 1 in 100 % yield.

This result illustrates the advantages of the electrochemical preparation of 1 in a series where the starting materials are costly. We are currently investigating the electrochemical preparation of disubstituted derivatives of 1 starting from 6.

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