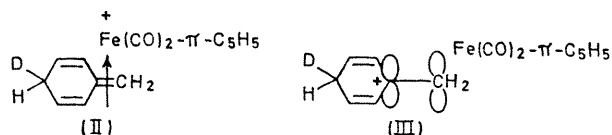


spectroscopy both of the product and of its *ortho*- and *para*-nitro-derivatives, to be as follows: *para*, $70 \pm 5\%$; *ortho*, $24 \pm 4\%$ (total); α -, $65 \pm 5\%$.

Clearly, deuteration of the ring does not necessarily result in cleavage of the carbon-iron bond, though it may be accompanied by such cleavage. The mechanism proposed is therefore analogous to that described for the deuteration of benzylicboronic acid in deuteriotartaric acid at 100° and is as shown in the Scheme.¹ A similar scheme may be drawn for the *ortho*-deuteration. However, these reactions are quite different from the deuteration of benzylmercury(II) chloride with DCl, in which only *ortho*-deuteration was detected.⁵



Under the conditions used in this work, toluene does not undergo detectable deuteration and anisole is deuteriated between 6 and 60 times more slowly than is the benzyldicarbonyl- π -cyclopentadienyliron. The lower figure is

based on the assumption that each cleavage of the carbon-iron bond is accompanied by deuteration of the ring, and the higher figure is based on the assumption that deuteration of the ring and carbon-iron bond cleavage are independent. It is evident that the positive charge on the benzene ring in the transition state for substitution is better accommodated by the group $-\text{CH}_2\text{Fe}(\text{CO})_2-\pi\text{-C}_5\text{H}_5$, as in (I), than it is by the methoxy-group. Such stabilisation may be a result of neighbouring-group participation *via* the π -complex (II), or by the 'vertical stabilisation'^{2,3} brought about by overlap of an appropriate filled orbital of the iron with the outer *p*-orbital of the partially quinonoid organic group [cf. (III)].

Whilst it is not possible directly to distinguish between these two possibilities for this reaction, only the vertical stabilisation, which does not involve significant alteration in the geometry of the carbon-iron bond, would be expected to influence markedly the position of the charge-transfer band with an acceptor such as tetracyanoethylene.² The appearance of a bright green charge-transfer complex between benzyldicarbonyl- π -cyclopentadienyliron and tetracyanoethylene is compatible with the vertical stabilisation.^{2,6}

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