Activation of Electrophilic Aromatic Substitution by a Methyleneiron Carbonyl Substituent

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Summary Deuteriation of the aromatic ring of benzyldicarbonyl-π-cyclopentadienyliron occurs more readily than does the deuteriation of anisole under comparable conditions; i.e., the group -CH₂Fe(CO)₂-π-C₅H₅ is more highly activating than is the methoxy-group in aromatic electrophilic substitution.

One of the most interesting of substituent effects in aromatic substitution is that of a number of non-transition metal containing groups of the type $-CH_2M$ (e.g., $M = SnMe_3$, $SiPh_3$, BX_2OH^- , etc.). These groups are unusually effective electron-donating substituents and spectroscopic, kinetic, and thermodynamic evidence suggests that some of them may be more effective than the methoxy-group.¹⁻³

We have suggested⁴ that a number of comparable transition-metal-containing groups, such as $-\text{CH}_2\text{Mn}(\text{CO})_5$, $-\text{CH}_2\text{Mo}(\text{CO})_3-\pi\text{-C}_5\text{H}_5$, $-\text{CH}_2\text{W}(\text{CO})_3-\pi\text{-C}_5\text{H}_5$ and $-\text{CH}_2\text{Co}(\text{CN})_5^{3-}$, from their influence on the basicity of pyridine, may also be strongly electron-donating. We now present evidence that the group $-\text{CH}_2\text{Fe}(\text{CO})_2-\pi\text{-C}_5\text{H}_5$ may activate the benzene ring towards electrophilic substitution, even though the carbon–iron bond is readily broken by a number of electrophilic reagents.

Thus, benzyldicarbonyl- π -cyclopentadienyliron decomposes in $\mathrm{CF_3CO_2D}$ (molar ratio, solute : solvent = 1:8) at room temperature ($t_1=ca.$ 10 min) to give toluene quantitatively. Up to four deuterium atoms were detected per molecule of product, and the extent of deuteriation of the toluene was shown by mass spectrometry and ¹H n.m.r.

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

Clearly, deuteriation 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 deuteriation of benzylboronic acid in deuteriotartaric acid at 100° and is as shown in the Scheme.1 A similar scheme may be drawn for the ortho-deuteriation. However, these reactions are quite different from the deuteriation of benzylmercury(II) chloride with DCl, in which only ortho-deuteriation was detected.5

Under the conditions used in this work, toluene does not undergo detectable deuteriation 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 carboniron bond is accompanied by deuteriation of the ring, and the higher figure is based on the assumption that deuteriation 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 $-CH_2Fe(CO)_2-\pi-C_5H_5$, 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 tetracyanoethylene is compatible with the vertical stabilisation.2,6

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