

THE FREE-RADICAL SUBSTITUTION OF FERROCENE AND THE

STABILITY OF FERROCENYLMETHYL RADICAL

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(i)

Statement

The work described in this thesis incorporates no material previously submitted for a degree in any University, except where due reference has been made.

(G. G. Vickery)

(ii)

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(iii)

Summary

The electron transfer between ferrocene and triphenylmethyl tetrafluoroborate has been shown to be moderately fast, and to be completely independent of the subsequent substitution of ferrocene.

Methyl-, isopropyl-, benzyl-, and phenyl-ferrocene have been mono-benzoylated by free-radical and electrophilic methods. For a particular ferrocene the isomer distributions of the products in both methods have been found to be identical. It was concluded that free-radical substitution of ferrocenium ion and electrophilic substitution of ferrocene pass through a common transition state. Some benzoylferrocenes which are inaccessible by electrophilic substitution may be synthesized by the free-radical route; the synthesis of *p*-benzoylferrocene in moderate yields was achieved.

The reaction of ferrocenium ion with alkyl radicals generated from triorganotin hydrides and alkyl halides was investigated. A value of $\underline{c.} 7 \times 10^5 \text{ l. mol}^{-1} \text{ s}^{-1}$ at 25°C was derived for the rate constant for ferrocenium ion substitution by alkyl radicals.

The stability of ferrocenylmethyl radical has been investigated by studying the products obtained from the one-electron reductions of a series of alkyl(ferrocenylmethyl) quaternary ammonium salts. The stability of this radical is intermediate between that of benzyl and t-butyl radicals. A method of synthesizing ferrocenylmethyamines from ferrocenylmethanol and amines has been explored, and shown to depend upon the pH of the solution, and on the nature of the amine.