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THE MECHANISM OF THE REACTION OF FERROCENE WITH FREE-RADICAL REAGENTS

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THE recent publication[2] of a mechanism for the arylation of ferrocene involving formation of a charge-transfer complex prompts us to report the results of our investigation into the reactions of ferrocene with free-radical reagents.

Ferrocene in benzene, when treated with benzoyl peroxide[3] or with t-butyl perbenzoate, gave ferric benzoate in high yield. Negligible quantities of carbon dioxide were evolved. The intermediate formation of ferricinium ion in these reactions was demonstrated by conducting the experiments in an apparatus designed to allow continuous extraction of the mixture with dilute sulphuric acid. Up to 78% of the ferrocene was then extracted as ferricinium ion and the yield of ferric benzoate was reduced accordingly.

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[2] Rosenblum, Howells, Banerjee and Bennett, J. Amer. Chem. Soc. 84, 2726 (1962).

[3] Pausacker, Austral. J. Chem. 11, 509 (1958).

In accord with previous observations[4] the reaction of ferrocene with N-nitrosoacetanilide in benzene gave phenylferrocene and diphenylferrocene. However, extraction of the mixture during the reaction with aqueous sulphuric acid yielded ferricinium ion and no substitution product could be detected.

The unreactivity of ferrocene towards attack by free radicals produced under conditions precluding concomitant formation of ferricinium ion was demonstrated by its recovery in high yield after treatment with azobisisobutyronitrile, with di-t-butyl peroxide in toluene,[5] or with benzenediazonium zincichloride and zinc powder in acetone-benzene.[6] Furthermore, addition of zinc powder inhibited the arylation of ferrocene by benzenediazonium sulphate. These results accord with earlier reports,[4] confirmed by us, that ferrocene does not react with free phenyl radicals generated from phenylazotriphenylmethane or phenylmagnesium bromide.

By contrast, ferricinium sulphate when treated with azobisisobutyronitrile in aqueous ethanol gave 2-cyano-2-ferrocenylpropane, m.p. 63-64° (Found: C, 66.4; H, 5.9; N, 5.6. Calc. for $C_{14}H_{15}FeN$: C, 66.4; H, 6.0; N, 5.5%), which was also synthesized by a conventional route. Since 1-cyano-1-methylethyl is a relatively stable radical, incapable of attacking lower aromatic hydrocarbons,[7] this reaction demonstrates the high reactivity of ferricinium ion towards free radicals.

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[4] Broadhead and Pauson, J. Chem. Soc. 367 (1955).

[5] Beckwith and Waters, J. Chem. Soc. 1001 (1957).

[6] Waters, J. Chem. Soc. 864 (1939); Norman and Waters, J. Chem. Soc. 167 (1958).

[7] Bickel and Kooyman, Rec. trav. chim. 71, 1137 (1952).

When a mixture of ferrocene and anthracene was treated with benzenediazonium sulphate in benzene-acetic acid the usual rapid evolution of nitrogen occurred but the only pure products isolated were 9-phenylanthracene and biphenyl, both indicative of the formation of free phenyl radicals. The same products were obtained when ferrocene and anthracene were heated with N-nitrosoacetanilide in benzene.

Our results, and those obtained by other workers, support the hypotheses that ferrocene is inert towards free alkyl or aryl radicals, that ferricinium ion is highly reactive, and that reactions of ferrocene with benzoyl peroxide, with N-nitrosoacetanilide, and with benzenediazonium ion,[8] involve intermediate formation of ferricinium ion (FcH = ferrocene).

$$\mathrm{FcH} + (\mathrm{PhCO_2})_2 \longrightarrow \mathrm{FcH}^+ + \mathrm{PhCO_2}^- + \mathrm{PhCO_2}\cdot$$

$$\mathrm{FcH} + \mathrm{Ph.N_2.OAc} \longrightarrow \mathrm{FcH}^+ + \mathrm{N_2} + \mathrm{Ph}\cdot + \mathrm{AcO}^-$$

$$\mathrm{FcH} + \mathrm{Ph.N_2}^+ \longrightarrow \mathrm{FcH}^+ + \mathrm{N_2} + \mathrm{Ph}\cdot$$

A one-electron-transfer reaction must also occur between ferrocene and benzoate radical,

$$\mathrm{FcH} + \mathrm{PhCO_2}\cdot \longrightarrow \mathrm{FcH}^+ + \mathrm{PhCO_2}^-$$

but further attack of benzoate radical on ferricinium ion effects disruption of the molecule. Alkylation of arylation of ferricinium ion probably involves the mechanism suggested by Little and Clark.[9]

$$\mathrm{FcH}^+ + \mathrm{R}\cdot \longrightarrow \left[\mathrm{FcRH}\right]^+ \longrightarrow \mathrm{FcR} + \mathrm{H}^+$$

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[8] Pauson, *Quart. Rev.* **9**, 391 (1955).

[9] Little and Clark, *J. Org. Chem.* **25**, 1979 (1960).

On the basis of these conclusions we reasoned that treatment of ferrocene with t-butyl perbenzoate in toluene should involve the following reactions.

$$FcH + PhCO_2OBu^t \longrightarrow FcH^+ + PhCO_2^- + Bu^tO\cdot$$

$$PhCH_3 + Bu^tO\cdot \longrightarrow PhCH_2\cdot + Bu^tOH$$

$$FcH^+ + PhCH_2\cdot \longrightarrow FcCH_2Ph + H^+$$

In fact there was obtained a moderate yield of benzylferrocene m.p. 74-75° (lit. m.p. 73-74°; 76°).[10]

Although the formation of a charge-transfer complex during the substitution step in the arylation reaction cannot be completely excluded, the results of our competition reactions with anthracene indicate that under these typical arylation conditions there is a relatively high concentration of free phenyl radicals. Also, conversion of 2,4-dinitrobenzenediazonium ion into *m*-dinitrobenzene on interaction with ferrocene,[4] requires reduction of the intermediate free 2,4-dinitrophenyl radical with a second molecule of ferrocene.

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[10] Hallam and Pauson, J. Chem. Soc. 3037 (1956); Rausch, Vogel and Rosenberg, J. Org. Chem. **22**, 903 (1957).