

FREE-RADICAL SUBSTITUTION OF FERRICINIUM ION THE MECHANISM OF THE ARYLATION OF FERROCENE

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Abstract—Formation of ferricinium ion is the primary step in reactions of ferrocene with *t*-butyl perbenzoate, benzoyl peroxide, and *N*-nitrosoacetanilide. Ferrocene is unaffected by treatment with free-radical reagents or arenediazonium salts under experimental conditions precluding formation of ferricinium ion. 1-Cyano-1-methylethyl radicals and benzyl radicals each react with ferricinium ion forming appropriately substituted ferrocenes. Experimental evidence supports the view that arylation of ferrocene with arenediazonium salts proceeds by attack of *free* aryl radicals on ferricinium ion. It is suggested that the relative ease of reaction of a substituted ferricinium ion with free radicals may be correlated with its reduction potential.

THE salient features of the free-radical chemistry of ferrocene may be summarized as follows. Ferrocene reacts readily with benzenediazonium ion in water, or organic solvents, yielding a mixture of mono- and diphenyl-ferrocenes.¹⁻⁴ Similar arylations occur with many substituted aromatic diazonium salts,¹⁻⁵ but addition of 2,4-dinitrobenzenediazonium sulphate to ferrocene results in the formation of 2,4-dinitrobenzene and ferricinium ion.¹ Aryl-substituted ferrocenes may also be prepared by treatment of ferrocene with arenediazoacetates in ether under Gomberg conditions⁶ or in cyclohexane;¹ pentaphenylferrocene has been obtained from one such reaction.^{6b} Arylation also occurs on addition of arenediazonium salts to ferricinium ion solutions,^{7,8} which, when prepared by the usual methods, contain traces of free ferrocene. However, the reaction is inhibited completely if ferrocene is removed beforehand by extraction of the ferricinium salt solution with ether.⁹

Ferrocene, when treated with *N*-nitrosoacetanilide in cyclohexane, yields a mixture of arylated products,¹ but no reaction occurs between ferrocene and free phenyl radicals derived from phenylazotriphenylmethane or from phenylmagnesium

¹ G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.* 367 (1955).

² M. Rosenblum, *J. Amer. Chem. Soc.* **81**, 4530 (1959).

³ M. Rosenblum, W. G. Howells, A. K. Banerjee and C. Bennett, *J. Amer. Chem. Soc.* **84**, 2726 (1962).

⁴ J. G. Mason and M. Rosenblum, *J. Amer. Chem. Soc.* **82**, 4206 (1960).

⁵ A. W. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, N. A. Simukova and O. V. Staravskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk* 638 (1957); E. G. Perevalova, N. A. Simukova, T. V. Nikitina, P. D. Reshetov and A. N. Nesmeyanov, *ibid.* 77 (1961).

^{6a} A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.* **97**, 459 (1954); ^{6b} A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *ibid.* **99**, 539 (1954); ^c A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, *ibid.* **102**, 535 (1955).

⁷ V. Weinmayr, *J. Amer. Chem. Soc.* **77**, 3012 (1955).

⁸ W. F. Little and A. K. Clark, *J. Org. Chem.* **25**, 1979 (1960).

⁹ G. D. Broadhead and P. L. Pauson, unpublished results quoted in ref. 12.

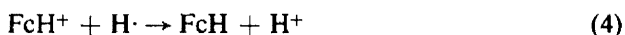
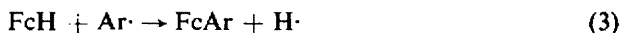
bromide.¹ Benzoyl peroxide was reported initially not to effect substitution of ferrocene,¹⁰ and Pausacker showed later that ferric benzoate is formed in good yield.¹¹

To account for these experimental observations various mechanisms have been advanced. Pauson has suggested that the primary step in the reaction of ferrocene with arenediazonium salts involves a one-electron transfer yielding ferricinium ion and arenediazonium radicals: the latter decompose spontaneously into nitrogen and free aryl radicals (FcH — ferrocene).¹²



This mechanism accounts satisfactorily for the ease with which the reaction proceeds under conditions milder than those normally required for non-catalytic decomposition of diazonium salts. It also explains why diazonium salts do not react with ferricinium ion in the absence of free ferrocene.

Pauson¹² has suggested that aryl radicals produced according to Eq. (2), or by thermal decomposition of diazoacetates, react directly with ferrocene. Hydrogen atoms formed in the substitution step reconvert ferricinium ion, generated in step (1), into ferrocene.



In reactions involving diazoacetates, hydrogen atoms would be removed, presumably by coupling with acetate radicals.



The successful arylation of ferrocene in cyclohexane, an active hydrogen-atom donor, has been interpreted as indicating that ferrocene is highly reactive towards attack by free radicals.¹² However, this view cannot be reconciled with the failure of ferrocene to react with free phenyl radicals generated from phenylazotriphenylmethane or from phenylmagnesium bromide.¹ Furthermore, it has been shown that substitution of aromatic compounds by a mechanism analogous to that of step (3) is energetically unfavourable.¹³ Two alternative explanations may be considered; that reactions of ferrocene with diazonium compounds proceed by an ionic mechanism or that they involve attack of free radicals on some reactive intermediate formed from ferrocene. Evidence to be presented here supports the latter hypothesis, the reactive intermediate being the ferricinium ion. This view conflicts with the statement¹² that ferricinium ion is much less reactive than ferrocene towards attack by free aryl radicals, but it is in accord with the suggestion of Little and Clark⁸ that ferricinium ion readily undergoes free-radical substitution as follows:



This mechanism has the virtue of proceeding through an intermediate complex analogous to that involved in radical substitution of other aromatic systems.¹³

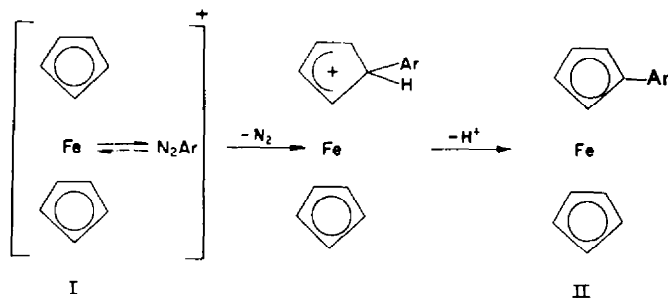
¹⁰ P. L. Pauson, *J. Amer. Chem. Soc.* **76**, 2187 (1954).

¹¹ K. H. Pausacker, *Austral. J. Chem.* **11**, 509 (1958).

¹² P. L. Pauson, *Quart. Rev.* **9**, 391 (1955).

¹³ C. Walling, *Free Radicals in Solution*, p. 482. J. Wiley, New York (1957).

In a recent paper³ Rosenblum *et al.* have discussed the mechanism of the arylation of ferrocene, and have concluded that ferrocene is relatively inert towards attack by free radicals. They suggest that the reaction proceeds through a reactive intermediate, namely, a charge-transfer complex (I), which decomposes in an intramolecular manner



yielding arylated product (II). The validity of this hypothesis rests mainly upon the relative amounts of mono- and di-substitution occurring when ferricinium ion is treated with various arenediazonium salts.⁷ We believe, however, that there is an acceptable alternative interpretation of these experimental results (*vide infra*).

We now describe a number of experiments designed to provide further evidence concerning the mechanism of the reaction of ferrocene with free-radical reagents. Initially, the reaction of ferrocene with *t*-butyl perbenzoate was investigated. When equimolar proportions of the reactants were heated in benzene the product was an insoluble brown powder consisting mainly of ferric benzoate mixed with a small amount of ferrous benzoate. No phenylferrocene could be detected and a negligible quantity of carbon dioxide was evolved. Benzoic acid, unchanged ferrocene, and intractable oils were isolated from the crude benzene-soluble product. Repetition of the reaction using an excess of peroxide afforded increased yields of ferric benzoate and benzoic acid. These results closely parallel those obtained by Pausacker¹¹ when he treated ferrocene with benzoyl peroxide. Having regard to the ease of oxidation of ferrocene to ferricinium ion^{12,14} it seems probable that both reactions proceed initially by transfer of an electron to the peroxide (R = PhCO or Bu^t).



The intermediate formation of ferricinium ion during the reaction of ferrocene with *t*-butyl perbenzoate was demonstrated by repeating the experiment in an apparatus designed especially to allow continuous extraction of the reaction mixture with dilute sulphuric acid. The aqueous extract contained ferricinium ion equivalent to 78% of the starting material: the yield of ferric benzoate was reduced accordingly.

The same technique was applied next to the reaction of ferrocene with benzoyl peroxide in benzene. Although its efficient extraction was hindered by the unexpected rapidity of the reaction, ferricinium ion was obtained in 23% yield and the amount of ferric benzoate isolated was much less than that reported by Pausacker.¹¹ No carbon dioxide was evolved from the reaction mixture.

A mechanism for the formation of ferric benzoate consistent with the experimental results involves disruption of the ferricinium ion by its reaction with *t*-butoxy or

¹⁴ M. Rausch, M. Vogel and M. Rosenblum, *J. Chem. Educ.* **34**, 268 (1957).

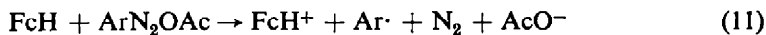
benzoate radicals according to equation (9; R = PhCO or t-Bu). Oxidation of ferrous to ferric ion by peroxide would then follow the normal course.¹⁵



In the case of the reaction using benzoyl peroxide, step (10) initiates a chain sequence, thus accounting for the unusual rapidity of the overall process. The cyclopentadienyl residues formed in step (9) are converted, presumably, by further attack of free radicals into the intractable oils isolated from our experiments.

The oxidation of ferrocene with benzoyl peroxide or with t-butyl hydroperoxide provides a convenient method for the preparation of solutions, or finely-divided suspensions, of ferric salts in organic solvents, for use as catalysts in various free-radical reactions.¹⁶

By analogy with step (9), we anticipated that a similar electron-transfer reaction should take place between ferrocene and arenediazoacetate.



This hypothesis was tested by studying the interaction of ferrocene and N-nitrosoacetanilide. The two reactants, when heated in benzene, gave phenylferrocene. However, when the experiment was repeated with continuous extraction of the reaction mixture with aqueous acid, 73% of the starting material was recovered and most of the remainder was converted into ferricinium ion. Phenylferrocene, although detected, was formed in very small yield. A complicating factor in this experiment was the conversion of the diazoacetate into diazonium salt and its subsequent extraction into the aqueous phase. Nevertheless, the results do not discord with the suggestion that the reaction of ferrocene with N-nitrosoacetanilide involves intermediate formation of ferricinium ion.

We next investigated free-radical reactions of ferrocene conducted under such conditions as to preclude formation of ferricinium ion. The failure of ferrocene to react with free phenyl radicals generated from phenylmagnesium bromide or phenylazotriphenylmethane¹ was confirmed. Although biphenyl was formed in the former reaction, presumably by attack of phenyl radicals on the benzene solvent, ferrocene was recovered in high yield from both experiments. Similarly, substitution products could not be detected after treatment of ferrocene with 1-cyano-1-methylethyl radicals derived from azobisisobutyronitrile,¹⁷ or with benzyl radicals formed by thermal decomposition of di-t-butyl peroxide in toluene.¹⁸ Of especial interest was the reaction of benzenediazonium zincchloride with zinc powder¹⁹ and ferrocene in acetone-benzene. Although biphenyl was detected no phenylferrocene was formed and ferrocene was substantially recovered. The presence of an excess of zinc powder also inhibited completely phenylation of ferrocene with benzenediazonium sulphate in aqueous acetic acid.

¹⁵ S. Hasegawa and N. Nishimura, *Bull. Chem. Soc. Japan* **33**, 775 (1960); S. Hasegawa, N. Nishimura and K. Miura, *ibid.* 1323 (1960).

¹⁶ A. L. J. Beckwith and B. S. Low, *J. Chem. Soc.* in press.

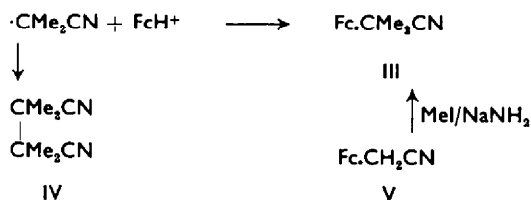
¹⁷ F. M. Lewis and M. S. Matheson, *J. Amer. Chem. Soc.* **71**, 747 (1949); C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.* 2661 (1949).

¹⁸ A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.* 1001 (1957).

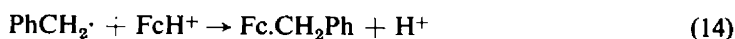
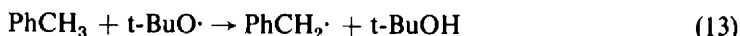
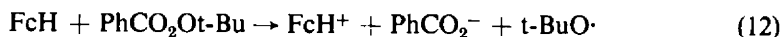
¹⁹ W. A. Waters, *J. Chem. Soc.* 864 (1939); R. O. C. Norman and W. A. Waters *ibid.* 167 (1958).

These results provide strong support for the hypothesis that ferrocene is inert towards attack by free radicals, and that substitution occurs only when intermediate formation of ferricinium ion is possible. We sought next to establish the validity of the accompanying corollary: that ferricinium ion is readily attacked by free radicals. Evidence in this regard had already come from reactions of ferrocene with benzoyl peroxide (*vide supra*) where the very low yields of carbon dioxide indicate that the rate of attack of benzoate radicals on ferricinium ion must be considerably faster than their decarboxylation.

When ferricinium ion, prepared by oxidation of ferrocene with sulphuric acid,⁷ was heated with azobisisobutyronitrile in aqueous ethanol under reflux it underwent substitution by 1-cyano-1-methylethyl radicals as was demonstrated by the isolation, in small yield, of 2-cyano-2-ferrocenylpropane (III) identical with a synthetic specimen. Since a control experiment revealed that ferricinium ion slowly decomposed under our original conditions, the substitution reaction was repeated at a lower temperature. A large excess of azo compound was employed, but the extent of its homolysis was calculated from the amount of nitrogen evolved, and the experiment was stopped when three molar equivalents of gas had been collected. The yield of substitution product based on unrecovered ferrocene was then 49%. No acetone cyanhydrin was detected in the crude product, and the free-radical character of the reaction was demonstrated by the isolation of a significant quantity of tetramethylsuccinonitrile (IV) formed by dimerisation of 1-cyano-1-methylethyl radicals. Authentic 2-cyano-2-ferrocenylpropane (III) was conveniently prepared by methylation of ferrocenyl-acetonitrile²⁰ (V) with sodamide and methyl iodide.



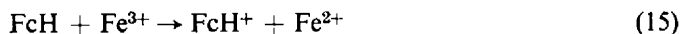
We anticipated that ferricinium ion would also readily undergo substitution by free benzyl radicals. However, the conduct of this reaction was beset by considerable experimental difficulties: attempts to prepare ferricinium salts in toluene solution proved fruitless. Eventually ferrocene was treated with *t*-butyl perbenzoate in toluene-acetic acid. We expected that the following reactions would occur:



In the event, we isolated both benzylferrocene and ferric benzoate. The formation of the latter may be ascribed to a cage-reaction between ferrocene and *t*-butoxy radicals according to equation (9; R = *t*-Bu). Accordingly, the experiment was

²⁰ D. Lednicer, J. K. Lindsay and C. R. Hauser, *J. Org. Chem.* **23**, 653 (1958).

repeated in the presence of an excess of ferric chloride which, we anticipated, would lead to ferrous-ion catalysed decomposition of the peroxide as follows:



The yield of benzylferrocene was then improved considerably notwithstanding losses due to its decomposition during chromatography.²¹

On the basis of these results, we conclude that ferricinium ion, unlike ferrocene, is readily attacked by free radicals. In an attempt to estimate its reactivity competitive reactions were conducted. As described in our preliminary communication²² 9-phenylanthracene and biphenyl, both indicative of the intermediate formation of free phenyl radicals, were detected when a mixture of anthracene and ferrocene in benzene-acetic acid was treated with benzenediazonium sulphate or with N-nitrosoacetanilide. The relative yields of phenylated products were more accurately estimated in later experiments when a mixture of anthracene and ferrocene was treated with benzenediazonium borofluoride in acetone-acetic acid. 9-Phenylanthracene, 9,10-diphenylanthracene, and phenylferrocene were isolated chromatographically, and the first two were also determined spectroscopically by the method previously employed with phenylphenanthrenes.²³

It was found that under these conditions ferrocene and anthracene are arylated approximately to the same degree. Similar results were obtained when the reaction was conducted in the presence of sodium acetate. Throughout these experiments the concentration of ferricinium ion formed by the appropriate electron-transfer reaction (I or II) must have been considerably less than that of anthracene, and we conclude, therefore, that ferricinium ion has reactivity towards attack by free radicals at least equal to anthracene, i.e. approximately 800 times greater than benzene.²⁴

The results of our competition experiments also strongly support the suggestion that the arylation of ferrocene proceeds through the agency of *free* phenyl radicals, a view which conflicts with the hypothesis³ that the reaction is mainly intramolecular. * It is pertinent, therefore, to re-examine the experimental evidence upon which the latter theory is based. Weinmayr⁷ studied the reaction of ferricinium ion with diazonium salts and found that *p*-nitrobenzenediazonium ion afforded mainly di-arylated product, whereas mono-arylated ferrocene was obtained exclusively when *p*-hydroxybenzenediazonium ion was employed. With benzenediazonium salt the reaction afforded both mono- and di-substituted products. According to Rosenblum *et al.*³ these results indicate that arylation involves reaction of the diazonium ion with the neutral species rather than with the cation, for in this way the extent of diarylation

* W. F. Little, K. N. Lynn and R. Williams [*J. Amer. Chem. Soc.*, **85**, 3055 (1963)] have reported recently that reactions of ferrocene with *o*-substituted arenediazonium salts in halohydrocarbon solvents yield ferrocenemonoaldehyde and other products the formation of which must be ascribed to attack by radicals derived from the solvent on ferrocene or ferricinium ion. Their results accord with the suggestion that interaction of ferrocene and arenediazonium ion initially produces *free* aryl radicals.

²¹ A. N. Nesmeyanov, I. I. Kritskaya and T. V. Antipina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk* 1777 (1962).

²² A. L. J. Beckwith and R. J. Leydon, *Tetrahedron Letters* No. 6, 385 (1963).

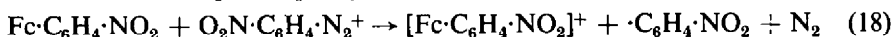
²³ A. L. J. Beckwith and M. J. Thompson, *J. Chem. Soc.* 73 (1961).

²⁴ M. Levy and M. Szwarc, *J. Amer. Chem. Soc.* **77**, 1949 (1955).

may be correlated with the effect of the known oxidation potentials⁴ upon the position of the following equilibrium.



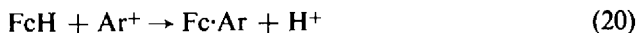
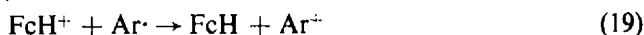
In our opinion this theory takes insufficient account of the fact that solutions of ferricinium salts prepared by Weinmayr's method contain only trace amounts of the neutral species. Having regard to the relationship between half-wave polarographic reduction potential and reactivity towards free radicals in the carbocyclic aromatic series,²⁵ we suggest that the ease of arylation of substituted ferricinium ions may be similarly correlated with appropriate reduction potentials. Weinmayr's arylation data may be satisfactorily interpreted according to this hypothesis. Thus, in the experiment using *p*-nitrobenzenediazonium salt the primary substitution product is converted, according to equation (18), into *p*-nitrophenylferricinium ion, which, having the more favourable reduction potential, competes effectively with the unsubstituted cation for further reaction with *p*-nitrophenyl radicals



It follows from this argument that reactions conducted under such conditions that ferrocene and its derivatives remain predominantly in the neutral form will yield amounts of mono- and di-substituted products different from those obtained by Weinmayr. Indeed, neutral ferrocene when treated with *p*-nitrobenzenediazonium chloride affords 64% of *p*-nitrophenylferrocene and 4% of bis-(*p*-nitrophenyl)ferrocene.^{6b} With *p*-methoxybenzenediazonium salt the yields of mono- and di-substituted ferrocene are each 7%.³

The unreactivity of neutral ferrocene towards attack by free radicals may also be interpreted in terms of its reduction potential, for it has been observed that ferrocene accepts an electron only with difficulty, and when it does so the molecule suffers complete disruption.²⁶

The arylation data is also explicable in terms of a mechanism involving an electron-transfer step (19) followed by electrophilic substitution (20).



Mechanistic analogy is provided by the Sandmeyer reaction where cupric ions, formed from cuprous ions by electron transfer to arenediazonium salt, are reduced back to cuprous ions by aryl radicals.²⁷ However, in the case of ferrocene and its derivatives, this type of mechanism appears improbable. The reaction of triphenylmethyl carbonium ion with ferrocene²⁸ involves electron-transfer in the direction opposite to that required by step (19) and a similar intramolecular transfer has been observed on treatment of ferrocenylmethanol with strong acid.²⁹ Moreover, the isolation of *m*-dinitrobenzene after interaction of *m*-dinitrobenzenediazonium sulphate with ferrocene possibly indicates that, in favourable cases, further reduction of aryl radicals

²⁵ F. A. Matsen, *J. Chem. Phys.* **24**, 602 (1956); A. L. J. Beckwith, D. Phil. Thesis, Oxford University (1956).

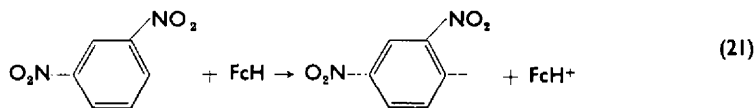
²⁶ D. S. Trifan and L. Nicholas, *J. Amer. Chem. Soc.* **79**, 2746 (1957).

²⁷ E. S. Gould, *Mechanism and Structure in Organic Chemistry* p. 729. Holt, Rinehart and Winston, New York (1959).

²⁸ M. F. Hawthorne, *J. Org. Chem.* **21**, 363 (1956).

²⁹ K. L. Rinehart, C. J. Michejda and P. A. Kittle, *J. Amer. Chem. Soc.* **82**, 3162 (1959).

to carbanions may occur. Finally, the complete absence of phenyl acetate from the



products of the reaction of ferrocene with phenyldiazonium ion in the presence of sodium acetate appears to preclude a mechanism involving carbonium ions.

EXPERIMENTAL

UV absorption spectra were determined in 95% ethanol. Adsorption chromatography was conducted on neutral alumina ("Woelm," activity I) or on acid-washed alumina ("Spence," type U.G.I.) using light petroleum and light petroleum-benzene as eluants. Paper chromatography was carried out on paper treated with dimethylsulphoxide²⁰ or on acetylated paper with the solvent system methanol-ether-water 4:4:1.²¹ Microanalyses were carried out by the C.S.I.R.O. and University of Melbourne Microanalytical Service.

Reaction of ferrocene with *t*-butyl perbenzoate

(a) Ferrocene (5.0 g, m.p. 174–175°) and *t*-butyl perbenzoate (5.2 g) in benzene (200 ml) were boiled under reflux (N₂ atm.). The mixture slowly turned brown, and after 2 hr, a precipitate began to form. Carbon dioxide (35 mg) evolved during the reaction was absorbed by soda-lime in a pre-weighed tube. After 14 hr the reaction mixture was cooled and filtered. The reddish-brown residue consisted of a mixture (2.7 g) of ferric benzoate with a little ferrous benzoate: it gave positive tests for the presence of both ferrous and ferric ion. Evaporation of the organic layer after shaking a sample (1.0 g) of the residue with ether and H₂SO₄ aq. gave benzoic acid (0.8 g. Required for ferric benzoate: 0.87 g).

The filtered reaction mixture was washed (with dil. H₂SO₄ and Na₂CO₃ aq.) Acidification of the alkaline extract afforded benzoic acid (0.7 g). Evaporation of the benzene solution gave a black residue which was separated chromatographically into ferrocene (2.9 g) and a series of brown, intractable, oily fractions.

(b) When the preceding experiment was repeated using *t*-butyl perbenzoate (15.7 g) and ferrocene (5.0 g), the products were benzoic acid (1.5 g) and ferric benzoate (5.6 g). Some ferrocene (0.7 g) was recovered.

(c) Ferrocene (4.0 g) and *t*-butyl perbenzoate (12.5 g) in benzene (200 ml) were heated (N₂ atm.) under reflux with 1N H₂SO₄ (ca. 200 ml) in a modified separating funnel. Whilst the mixture was stirred the aqueous layer was run off and continuously replenished with acid at the same rate, namely 10 ml/min for the first 6 hr, 3 ml/min for the next 5 hr, and 1.4 ml/min for the last 3 hr. The blue, ferricinium ion solution collected in this way was reduced (with TiSO₄ aq.) and then extracted with ether. The aqueous layer gave a positive test for the presence of ferrous ion. Benzoic acid (4.0 g) was isolated (extraction with Na₂CO₃ aq.). Evaporation of the ethereal solution afforded ferrocene (3.1 g, 78%).

When the benzene solution from the reaction mixture was filtered a residue of crude ferric benzoate (1.1 g, 12%) was collected. Extraction of the filtrate (Na₂CO₃ aq.) gave benzoic acid (1.4 g, Total 5.4 g, 69%). Ferrocene (trace) and intractable oil were separated chromatographically from the residue obtained by evaporation of the benzene layer.

Reaction of ferrocene with dibenzoyl peroxide

Ferrocene (4.0 g) and dibenzoyl peroxide (7.8 g) were brought into reaction whilst extracted with aqueous acid following the method of the preceding experiment. Although heating was continued for 7 hr, the formation of ferricinium salt appeared to be complete after 45 min. Crude ferric benzoate (1.7 g, 19%) and benzoic acid (3.6 g) were isolated as before, and ferrocene (0.63 g) was recovered chromatographically from the residue obtained by evaporation of the benzene solution. Chromatography of the crude product from reduction of the aqueous extract (with TiSO₄) afforded ferrocene

²⁰ A. N. de Belder, E. J. Bourne, and J. B. Pridham, *Chem. & Ind.* 996 (1959).

²¹ T. M. Spotswood, *J. Chromatog.* 2, 90 (1959).

(0.9 g, 23%) and a trace of an unidentified pink substance having UV absorption max at 232, 269, 333, and 456 μ . No carbon dioxide was evolved during the reaction.

Reaction of ferrocene with N-nitrosoacetanilide

(a) N-Nitrosoacetanilide (2.6 g) in benzene (50 ml) was added to a stirred solution of ferrocene (3.0 g) in benzene (50 ml) and the mixture was maintained at 50° (under N_2) until evolution of gas commenced. The mixture was then allowed to cool to room temp. and stirring was continued for 8 hr. Extraction of the reaction mixture with dil. H_2SO_4 gave a blue solution of ferricinium salt, which, when reduced (with $TiSO_4$) yielded ferrocene (10 mg). The dark residue (4.0 g) obtained by evaporation of the benzene layer was adsorbed on alumina and chromatographed. Elution of the column with light petroleum afforded consecutively biphenyl (75 mg), ferrocene (1.2 g), phenylferrocene (0.6 g), m.p. 109–110° (lit.¹ m.p. 109–110°), and 1,1'-diphenylferrocene (0.2 g), m.p. 154–155° (lit.¹ m.p. 154°). The UV absorption spectra of phenyl- and 1,1'-diphenylferrocene were in accord with published data.²⁹

(b) The preceding experiment was repeated whilst continually extracted with dil. H_2SO_4 as described above. The ferricinium ion solution when reduced (with $TiSO_4$) afforded ferrocene (0.6 g, 20%). The benzene solution, upon evaporation and chromatography of the residue, gave ferrocene (2.2 g) and a trace of phenylferrocene.

A separate experiment indicated that dil. H_2SO_4 rapidly extracts N-nitrosoacetanilide as benzenediazonium ion from benzene solution.

Attempted reaction of ferrocene with phenyl radicals

(a) *Phenyl radicals derived from phenylmagnesium bromide.* Anhydrous $CoCl_2$ (0.12 g) was added to ferrocene (11.6 g) in benzene (100 ml) and the mixture was stirred (under N_2) while phenylmagnesium bromide (prepared from 9.8 g of bromobenzene) in ether (100 ml) was added dropwise during 1 hr. The mixture was then boiled under reflux for 1 hr, and set aside overnight at room temp, NH_4Cl aq. was then added to the mixture, and the organic layer was separated, washed, dried, and evaporated. Fractional crystallization of the residue from pentane gave ferrocene (10.5 g) and biphenyl (0.3 g). Phenylferrocene was not detected spectroscopically, or by paper chromatography. The aqueous washings contained neither ferrous nor ferric ion.

(b) *Phenyl radicals derived from phenylazotriphenylmethane.* Ferrocene (2.5 g) and phenylazotriphenylmethane (9.5 g) in benzene (200 ml) were boiled under reflux (N_2 atm.) for 5 hr, and the mixture was then evaporated under red. press. Chromatography of the residue afforded ferrocene (2.4 g).

(c) *Phenyl radicals derived from benzenediazonium zincchloride and zinc powder.* Benzenediazonium zincchloride (23.7 g) was added in portions to a vigorously stirred suspension of Zn powder (100 g), $CaCO_3$ (10 g) and ferrocene (8 g) in acetone (250 ml) and benzene (250 ml) at room temp. Stirring was continued for 10 hr. The suspension was then filtered and the residue was washed with acetone. Chromatography of the residue obtained by evaporation of the filtrate afforded ferrocene (7.5 g) but no phenylferrocene.

Attempted reaction of ferrocene with benzenediazonium sulphate in the presence of zinc powder

The method¹ for the preparation of phenylferrocene by treatment of ferrocene (3 g) with benzenediazonium sulphate (prepared from 1.5 g of aniline) in acetic acid (100 ml) was conducted in the presence of Zn powder (25 g). Negligible quantities of phenylferrocene were formed and ferrocene (2.9 g) was recovered.

Attempted reaction of ferrocene with 1-cyano-1-methylethyl radicals

Ferrocene (2.5 g) and azodiisobutyronitrile (4.45 g) in ethanol (150 ml) were boiled under reflux (N_2 atm.) for 4 hr, and a portion (100 ml) of the solvent was then removed by distillation. Ferrocene (1.2 g) was collected by filtration of the cooled reaction mixture. After evaporation of the mother liquor the residue was separated chromatographically into ferrocene (total: 2.1 g) and tetramethylsuccinonitrile (1.9 g), m.p. and mixed m.p. 168–169°.

²⁹ R. T. Lundquist and M. Cais, *J. Org. Chem.* **27**, 1167 (1962).

Attempted reaction of ferrocene with benzyl radicals

Ferrocene (7.0 g) and di-*t*-butyl peroxide (5.6 g) in toluene (200 ml) were heated under reflux (N_2 atm.) for 7 days. The reaction mixture was then evaporated under red. press. and the residue was fractionally crystallized from methanol yielding ferrocene (5.5 g) and bibenzyl (1.5 g), m.p. and mixed m.p. 52° . Benzylferrocene could not be detected.

When the experiment was repeated using ferrocene (4.0 g) and di-*t*-butyl peroxide (20 g) the products were bibenzyl (6.2 g) and ferrocene (2.5 g).

Reaction of ferricinium ion with 1-cyano-1-methylethyl radicals

(a) Conc. H_2SO_4 (25 g) was added to ferrocene (5.0 g) with shaking and cooling in ice. The resultant violet solution was set aside at room temp overnight and then diluted with cold ethanol (300 ml). Azodiisobutyronitrile (8.9 g) was added, and the mixture was then boiled under reflux (N_2 atm.) for 4 hr. After addition of water to the cooled reaction mixture, the brown precipitate (3.2 g) was collected, adsorbed on alumina, and chromatographed. Elution of the column with light petroleum gave ferrocene (2.1 g), an unidentified yellow crystalline substance (3 mg), m.p. $104-105^\circ$, and 2-cyano-2-ferrocenylpropane (0.4 g), which crystallized from light petroleum in yellow needles, m.p. $63-64^\circ$ (Found: C, 66.4; H, 5.9; N, 5.6. $C_{14}H_{13}FeN$ requires: C, 66.4; H, 6.0; N, 5.5%), λ_{max} 322 (ϵ 107) and $436 m\mu$ (ϵ 77), ν_{max} (CCl_4) 1280 and $2220 cm^{-1}$.

The filtrate from the reaction mixture was concentrated by evaporation under red. press. and the residue was extracted with benzene. The extract was washed (Na_2CO_3 aq.), dried, and evaporated. Fractional crystallization of the residue from pentane gave tetramethylsuccinonitrile (0.3 g), m.p. and mixed m.p. $169-170^\circ$, and crude ferrocene (1.5 g). Acetone cyanhydrin was not detected. The aqueous fraction from the reaction mixture, when reduced (with $TiSO_4$) afforded ferrocene (0.8 g).

(b) Azodiisobutyronitrile (17.2 g) was added to an aqueous ethanolic solution of ferricinium ion, prepared from ferrocene (5.0 g) as in the preceding experiment, and the mixture was maintained at 70° in an apparatus connected to a gas burette for 4.5 hr during which time approximately three molar equivalents (1,800 ml) of N_2 were evolved. The cooled reaction mixture was then reduced (with $TiSO_4$) and extracted with ether. Chromatography of the material obtained from the ether extract gave ferrocene (2.6 g), 2-cyano-2-ferrocenylpropane (1.6 g), and tetramethylsuccinonitrile (6.4 g).

2-Cyano-2-ferrocenylpropane

(Ferrocenylmethyl)trimethylammonium iodide³³ prepared by treatment of the product from ferrocene and N,N,N',N' -tetramethyldiaminomethane with methyl iodide, was converted into ferrocenylacetone nitrile.³⁰ The foregoing nitrile (11.0 g) in ether (100 ml) was added to sodamide (prepared from 1.3 g Na) in liquid ammonia (100 ml) with stirring, followed by methyl iodide (7.5 g). After evaporation of the ammonia the residual ethereal solution was boiled under reflux for 2 hr, then cooled, washed with water, and evaporated. Attempts to purify the residual crude 1-cyano-1-ferrocenylethane (8.4 g) were unsuccessful, and a sample (6.9 g) was therefore remethylated as above. Chromatography of the crude product afforded 2-cyano-2-ferrocenylpropane (4.3 g) as yellow needles, m.p. and mixed m.p. $63-64^\circ$.

Reaction of ferricinium ion with benzyl radicals

(a) *t*-Butyl perbenzoate (15.7 g) was added during 6 hr to a stirred solution of ferrocene (5.0 g) and anhydrous $FeCl_3$ (5.3 g) in toluene (130 ml) and acetic acid (65 ml), and the mixture was then stirred for a further 7 hr at 70° (in N_2 atm.). After filtration to remove iron salts the cooled reaction mixture was treated (with $TiSO_4$) and extracted with ether. Evaporation of the extract afforded a residue which was separated by crystallization from benzene and by chromatography into ferrocene (0.8 g), benzoic acid (1.8 g), and benzylferrocene (1.3 g), which crystallized from aqueous ethanol in golden plates, m.p. $74-75^\circ$ (lit.³⁴ m.p. $73-74^\circ$; 76°). (Found: C, 73.75; H, 5.9%; mol. wt. (Rast),

³³ J. K. Lindsay and C. R. Hauser, *J. Org. Chem.* **22**, 355 (1957); J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.* 656 (1958).

³⁴ B. F. Hallam and P. L. Pauson, *J. Chem. Soc.* 3037 (1956); M. Rausch, M. Vogel and H. Rosenberg *J. Org. Chem.* **22**, 903 (1957).

268. Calc. for $C_{17}H_{16}Fe$: C, 73.9; H, 5.85%; mol. wt. 276.) A mixture (150 mg) of unidentified substituted ferrocene derivatives was detected by thin-film chromatography. Extensive oxidative degradation of products occurred during column chromatography. Similar oxidation has been noted previously.²¹

(b) Ferrocene (5 g) in toluene (200 ml) was treated with *t*-butyl perbenzoate (22.3 g) by dropwise addition (ca. 1 hr) and the mixture kept at 70–80° with stirring for 6 hr under N_2 . The reaction mixture was allowed to stand overnight.

The mixture on filtration yielded ferric benzoate (4.0 g). The mother liquor, after treatment by the usual working up procedure, yielded ferrocene (400 mg) and benzylferrocene (100 mg).

Competitive arylation of ferrocene and anthracene

(a) Ferrocene (0.9 g) in acetone (40 ml) was added dropwise with stirring to benzenediazonium borofluoride (0.9 g) suspended in a solution of anthracene (0.5 g) in acetone (80 ml). After the addition (30 min) the reaction mixture was stirred for a further 30 min and diluted with water. The mixture was then extracted with ether, and the ethereal layer was washed several times with $FeCl_3$ in 6N H_2SO_4 to remove ferrocene and its derivatives in the cationic form. After washing (with Na_2CO_3 aq.) the ethereal solution was evaporated and the residue was purified by passage through a short alumina column. A sample (15 mg) of the eluted material (0.58 g) was chromatographed on acetylated cellulose using ethanol–benzene–water (17:4:1) as eluant. The fractions obtained were estimated spectroscopically to contain anthracene (6.3 mg) and 9-phenylanthracene (3.2 mg). Chromatography on alumina of the remainder of the material afforded anthracene (150 mg) and 9-phenylanthracene (80 mg).

The aqueous solution of ferricinium ion and its derivatives was reduced (with $TiSO_4$) and extracted with ether. Chromatography of the residue obtained by evaporation of the ether extract gave ferrocene (120 mg) and phenylferrocene (100 mg).

(b) Ferrocene (0.9 g) and anhydrous sodium acetate (0.4 g) in glacial acetic acid (40 ml) were added to benzenediazonium borofluoride (0.9 g) and anthracene (0.5 g) in acetone (80 ml) and the mixture was worked up as in the preceding experiment. The material extracted (with $FeCl_3$ aq.) was separated chromatographically into ferrocene (0.7 g) and phenylferrocene (32 mg). A sample (6.1 mg) of the ether-soluble material when chromatographed on acetylated cellulose gave anthracene (0.9 mg), 9-phenylanthracene (3.6 mg) and 9,10-diphenylanthracene (0.1 mg). The remainder was separated chromatographically into anthracene (102 mg), 9-phenylanthracene (186 mg), and 9,10-diphenylanthracene (6 mg). The crude product of this reaction showed no IR absorption in the carbonyl region: the absence of phenyl acetate was thus indicated.

When the foregoing experiment was repeated in the absence of anthracene the products were ferrocene (410 mg), phenylferrocene (62 mg), and 1,1'-diphenylferrocene (52 mg).

(c) The reaction of ferrocene (3.0 g) with *N*-nitrosoacetanilide (2.6 g), described above, was repeated in the presence of anthracene (3.0 g). 9-Phenylanthracene (0.25 g) was isolated chromatographically from the crude product which also contained biphenyl and unchanged starting materials all of which were detected by UV spectroscopy and chromatography.

(d) When ferrocene (4 g) and anthracene (4 g) in benzene (100 ml) and glacial acetic acid (100 ml) were treated with aqueous benzenediazonium sulphate (from 2 g of aniline) there was obtained a complex mixture of products, which could not be quantitatively separated into its constituents. However, small pure samples of biphenyl and 9-phenylanthracene were isolated.

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