Ferrocene Derivatives. Part 26.[1] The Photolysis of Halogenoferrocenes in Aromatic Solvents

Christopher Imrie, Derek C. Nonhebel* and Peter L. Pauson*
Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow G1 1XL, Scotland

Photolysis of iodoferrocene is shown to be a useful source of ferrocenyl radicals. When these substitute arenes the ratios of arylferrocene isomers resemble the ratios of isomeric biphenyls obtained with aryl radicals. Both the high proportion of *meta*-isomers obtained when strongly electron-withdrawing groups are present and the small proportion of side-chain attack on toluene mark ferrocenyl as an electrophilic radical, intermediate in this respect between phenyl and 4-nitrophenyl. Bromoferrocene and diferrocenylmercury are also briefly examined as sources of the ferrocenyl radical.

Ferrocenyl and other ferrocene-derived radicals have been implicated as intermediates in a variety of reactions, but there has been no systematic study of these or related organometallic radicals. We have set outselves the objective of finding efficient methods of generating ferrocenyl, ferrocenylmethyl and ferrocenoyl radicals and analogous radicals derived from other transition-metal π-complexes and of studying their chemical behaviour, especially in comparison with the corresponding benzene-derived radicals. As a first step towards this goal we describe here the photolysis of iodo- and bromo-ferrocene in several aromatic solvents.

Photolysis of halogenobenzenes is commonly employed to generate aryl radicals and, by analogy, ferrocenyl radicals have been assumed to be involved in previous studies of the photolysis of halogenoferrocenes. These include a study of their photolysis in alcoholic–aqueous media[2] which yields both alkoxyferrocene and ferrocene (no discussion of mechanism was included in this paper) and a brief study of the photolysis of iodoferrocene in cyclohexane, benzene and toluene.[3] Formation of bibenzyl in the last solvent is significant evidence for radical intermediates, but no isomer ratio is reported for the tolylferrocenes, the major products of the reaction (50%). The formation of ferrocene in an amount (24%) substantially in excess of the bibenzyl (9%) is most readily explained by processes also occurring with other arenes which are discussed below.

We describe here the results of a more detailed study of the photolysis of halogenoferrocenes in arenes in which, in addition to benzene and toluene, we have employed *tert*-butylbenzene, anisole, chlorobenzene, benzonitrile and benzotrifluoride. All yield mixtures of the *ortho*-, *meta*- and *para*-substituted arenes which were separated from the other products and, where possible from each other, by GLC. Preliminary separation of the arylferrocenes from the other products by alumina column chromatography was also used in some cases. All arylferrocenes were identifield by GLC comparison with authentic samples prepared by standard methods.[1,4–6] The principal results are summarised in Table 1 and, for selected cases compared with arylation reactions of the same arenes in Table 2.

The results strongly support the previous assumption[3] that ferrocenyl radicals are involved. Both the formation of bibenzyls from toluene and from *p*-xylene and the isomer ratios are clearly incompatible with the results expected for electrophilic substitution, but do suggest that ferrocenyl radicals are relatively electrophilic. The latter point is perhaps most strikingly illustrated by the enhanced proportion of *meta* substitution of both benzonitrile and benzotrifluoride when compared with phenylation of the same arenes (Table 2). In

addition to the arenes listed in Table 1, we also examined chlorobenzene and *tert*-butylbenzene but were unable to separate or estimate the proportions of *ortho*- and *meta*-isomers. However the readily separated *para*-isomers constitute only 10 and 23% of the corresponding arylferrocenes, values which are again incompatible with electrophilic attack. They compare with 16[7]–18%[8] of the *p*-chlorobiphenyl and 27%[9] of *tert*-butylbiphenyl obtained from free-radical phenylation of the same arenes using dibenzoyl peroxide. In the case of chlorobenzene, electrophilic ferrocenylation has been observed under Friedel–Crafts conditions[10] and found to give *para*- and *ortho*-isomers in approximately 3:2 ratio with no observed *meta*-isomer. Toluene by similar treatment gave a *ca.* 1:1 ratio of *ortho*- and *para*-isomers, again with no detected *meta*-substitution and of course no bibenzyl.

The formation of ferrocene in the photolytic ferrocenylations is thought to be due to one or both of the processes shown in eqns. (1) and (2), the former being considered more likely.

$$FcI \xrightarrow{hv} Fc\bullet + I\bullet$$

$$Fc\bullet + HI \longrightarrow FcH + I\bullet \quad (1)$$

$$(2)$$
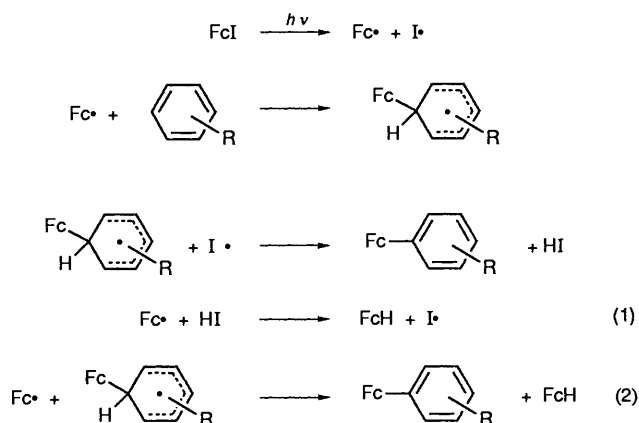
Hexafluorobenzene cannot yield ferrocene by such reactions, accounting for the absence of ferrocene in this case. Hydrogen abstraction from the methyl groups must account for the greatly increased ferrocene yields from toluene, *p*-xylene and also anisole. The availability of two methyl groups for such abstraction from *p*-xylene accounts for the greatly reduced ring substitution; the observed yield of 4,4'-dimethylbibenzyl closely matches the enhanced ferrocene yield in this case. The relatively low bibenzyl/ferrocene ratio in the case of toluene is more difficult to account for and it is not clear why our value for the yield of bibenzyl is only half the previously reported[3] figure (9%). It may be relevant to note that in the reaction of phenyl radicals with cumene[11] the bicumyl/benzene ratio is much

Table 1 Yields of products obtained by photolysis of iodoferrocene (100 mg) in arenes (20 cm³)

| Arene | Recovered iodoferrocene (%) | Yield of ferrocene^a (%) | Yield of arylferrocenes^a (%) | Isomers distribution (%) of arylferrocenes | | |
				o	m	p
PhCF₃	40–41	3	44–45	24–25	56–57	19
PhOMe	47	20	50–51	56–59	16	24–25
PhCN^b	6	9	44	55	32	13
PhMe	46–50	23–30	36–39^c	60–64^d	21–22	15–18
1,4-C₆H₄Me₂	1–2	24–30	7–13^e	—		
C₆F₆^f	45	—	32			

^a Yield based on unrecovered ferrocene. The range quoted represents the variation between two or more experiments. An iron-containing black solid (*ca.* 10 mg) was also obtained in each case. ^b A less efficient light source was used: single experiment. ^c Bibenzyl (4–5%) was also formed (calcd. on the basis 2FcI → PhCH₂CH₂Ph). ^d By NMR spectroscropy: we failed to separate the *o*-/*m*- mixture by GLC (GLC estimate indicated 88:12 (*o* + *m*)/*p*). ^e 4,4′-Dimethylbibenzyl (12–15%) was also formed. ^f Single experiment.

Table 2 Comparison of isomer ratios for substitution of anisole, benzonitrile and benzotrifluoride by ferrocenyl and by aryl radicals

| Arene | Radical | Radical source | Isomer distribution (%) | | | Ref. |
			o	m	p	
PhOMe	Fc	FcI/*hv*	59.5	16	24.5	This work
PhOMe	Ph	PhI/*hv*	71.5	15	13.5	13
PhOMe	Ph	PhN(NO)Ac	69	18	13	14
PhOMe	Thiazol-2-yl	2-IC₃H₂NS/*hv*	63	14	23	13
PhOMe	4-NO₂C₆H₄	4-NO₂C₆H₄N(NO)Ac	72	12	16	14
PhOMe	4-MeOC₆H₄	4-MeOC₆H₄N(NO)Ac	69	19	12	15
PhCN	Fc	FcI/*hv*	55	32	13	This work
PhCN	Ph	(PhCO₂)₂	60	10	30	16
PhCN	Ph	(PhCO₂)₂	52.3	17.4	30.3	8
PhCF₃	Fc	FcI/*hv*	24.5	56.5	19	This work
PhCF₃	Ph	(PhCO₂)₂	29	41	30	17

lower when iodobenzene is used as radical source than when dibenzoyl peroxide is employed. It must also be noted that in all the photolytic reactions of iodoferrocene studied by us the identified products account for 70% or less of the iodoferrocene decomposed so that other processes must also be occurring.

The low level of side-chain compared to nuclear attack on toluene constitutes further evidence for the electrophilic nature of the ferrocenyl radicals, a clear relation having been established in the case of aryl radicals for which the yields of bibenzyl decrease sharply with increasing electrophilicity. Typical bibenzyl yields are 47% for *p*-methoxyphenyl,[12] 24% for phenyl,[8] 11% for *p*-chlorophenyl[12] and none for *p*-nitrophenyl[12] radicals. In an experiment involving photolysis of iodoferrocene in an equimolar mixture of benzene and trifluoromethylbenzene, attack on the former predominated as expected of an electrophilic radical. The electrophilicity of ferrocenyl radicals is certainly remarkable since in other respects, notably the ease of electrophilic substitution, the ferrocene nucleus behaves as a very electron-rich system.

Several other potential sources of ferrocenyl radicals were also examined. Photolysis of bromoferrocene was found to be a much less efficient source, but the isomer proportions of the resultant arylferrocenes were identical within the limits of estimation to those recorded in Table 1 for iodoferrocene.

Thermolysis of diferrocenylmercury in a range of arene solvents leads to the puzzling result that although toluene yields bibenzyl, the major product in all cases is ferrocene and arylferrocenes are completely absent or present in trace amounts only. This is true even in hexafluorobenzene in which a 45% yield of ferrocene was obtained. Moreover in [²H₈]-toluene diferrocenylmercury yields C₁₀H₁₀Fe containing only 15% of C₁₀H₉DFe. The formation of ferrocene in these reactions must proceed by a mechanism not involving truly

free ferrocenyl radicals. One possibility is an intramolecular H transfer of the type shown below.* The resultant strained
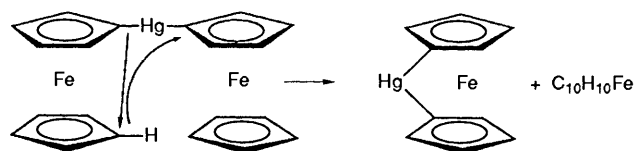
mercurioferrocenophane would probably polymerise. Nesmeyanov *et al.*[18] had previously reported that thermolysis of diferrocenylmercury in tetrachloromethane produces ferrocene and chloromercuriferrocene (but not chloroferrocene) a result which we have confirmed and which is consistent with the behaviour in arenes.

Photolysis of diferrocenylmercury in arenes did yield small amounts of arylferrocenes, but had to be conducted at high

---

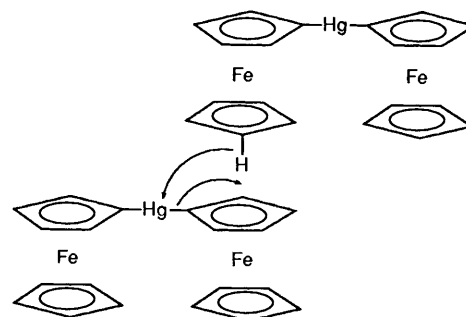* A referee has suggested the following alternative.

Table 3 New arylferrocenes (FcAr)

Ar	M.p. (T/°C)	δ C$_5$H$_5$	C$_5$H$_4$	Aryl	Analysis (%) Found C	H	Calc. C	H	Formula
4-CF$_3$C$_6$H$_4$	140–142	4.07(s)	4.10(t), 4.70(t)	7.6 (br s)	62.0	4.0	61.85	4.0	C$_{17}$H$_{13}$F$_3$Fe
2-CF$_3$C$_6$H$_4$	80–82	4.15(s)	4.30(t), 4.58(t)	7.7(m)	61.5	3.6	61.85	4.0	C$_{17}$H$_{13}$F$_3$Fe
3-NCC$_6$H$_4$	98–100	4.01(s)	4.35(t), 4.60(t)	7.5(m)	71.0	4.4	71.1	4.6	C$_{17}$H$_{13}$FeN
2,5-Me$_2$C$_6$H$_3$	58–60	4.13(s)	4.30(t), 4.48(t)	7.25(m)	74.8	6.3	74.5	6.25	C$_{18}$H$_{18}$Fe

Table 4 Decomposition of diferrocenylmercury in arenes

Arene	Products (%) of thermal reaction at 220 °C Unchanged Fc$_2$Hg	FcH	FcAr	Other	Products of irradiation under reflux T/°C	Unchanged Fc$_2$Hg	FcH	FcAr	Other
C$_6$H$_6$					80	27.5	11	19	
PhOMe	0	41	Trace		154	20	13	3	
PhMe	0	43	0	7[a]					
PhCF$_3$	0	45	Trace		102	17.5	10	1	
PhCN					188	0	30	0	
p-C$_6$H$_4$Me$_2$	45[b]	26	0	1[c]	138	64	16	1	3[c]
C$_6$F$_6$	0	45	0						

[a] Bibenzyl. [b] From reaction under reflux. [c] 4,4'-Dimethylbibenzyl.

temperature because of the low solubility of diferrocenylmercury; the observed products are therefore presumably largely those of thermal processes occurring in competition with photochemical processes.

Experimental

All reactions were carried out under nitrogen. Neutralised alumina was used for column chromatography.

The arylferrocenes required for chromatographic and spectral comparison with our products were prepared by literature methods[4–6,19] and had properties consistent with those reported. When the arylations were carried out in homogeneous media with acetic acid[4] or acetone[6] as organic component, the yields were generally poor. The ether–water systems employed by Nesmeyanov et al.[5] and in our recent syntheses of o-cyano- and o-nitro-phenylferrocene[1] should probably always be employed. Properties and analyses of four new arylferrocenes are collected in Table 3.

Iodoferrocene was prepared[20] from chloromercurioferrocene and had m.p. 48 °C (lit.,[21] m.p. 49–49.5 °C), v_{max}(KBr)/cm^{-1} 3090, 1600–1700, 1410, 1100, 1020, 1000 and 820; δ(CDCl$_3$) 4.33 and 4.00 (each 2 H, t, C$_5$H$_4$) and 4.10 (5 H, s, C$_5$H$_5$) (Found: C, 38.7; H, 2.7. Calc. for C$_{10}$H$_9$FeI: C, 38.5; H, 2.9%).

Bromoferrocene obtained (68% yield) by the literature method[22] had m.p. 32 °C (lit.,[22] m.p. 31–32 °C), v_{max}(KBr)/cm^{-1} 3100, 1405, 1375, 1150, 1100, 1000, 870 and 805; δ(CDCl$_3$) 4.08 and 4.42 (each 2 H, t, C$_5$H$_4$) and 4.24 (5 H, s, C$_5$H$_5$) (Found: C, 45.6; H, 3.4. Calc. for C$_{10}$H$_9$BrFe: C, 45.5; H, 3.4%).

Photolysis of Iodoferrocene in Arenes. General Procedure.— Iodoferrocene (0.10 g, 0.3 mmol) and the arene (20 cm^3) were placed in an externally water-cooled Pyrex reactor surrounding a 125 W medium pressure mercury arc lamp. After irradiation for 5 h the solutions were filtered and analysed by GLC usually using 2 m columns of 5% Carbowax on Chromosorb G in the temperature range 150–220 °C. (Alternative column packings were 5% FFAP on Chromosorb G or Apiezon). To ascertain

yields biphenyl was added to aliquots of the solution and peak areas were estimated for all components. The relative response for biphenyl was checked for reference samples under each set of conditions. The results are in Tables 1 and 2.

Thermal Decomposition of Diferrocenylmercury in Arenes.— (a) *Toluene and* [^{2}H$_8$]*toluene.* An ampoule containing diferrocenylmercury (50 mg, 0.088 mmol) and toluene (2 cm^3) was degassed by three freeze–thaw cycles and sealed *in vacuo.* After the mixture had been heated to 220 °C for 24 h, GLC analysis showed the formation of ferrocene (18 mg, 55%), bibenzyl (11%) and a dark solid residue (3 mg). The same procedure repeated with C$_7$D$_8$ yielded ferrocene (14 mg, 43%) shown by mass spectrometry to contain 85% [^{2}H$_0$]ferrocene and 15% [^{2}H$_1$]ferrocene and [^{2}H$_{14}$]bibenzyl (6%).

(b) *Other arenes.* The same procedure but using diferrocenylmercury (20 mg) and arene (5 cm^3) was employed; the results are in Table 4.

Photolysis of Diferrocenylmercury in Arenes.—Solutions of diferrocenylmercury (0.2 g, 0.35 mmol) in the arene (100 cm^3) were irradiated with a 250 W medium pressure mercury lamp for 24 h without cooling. GLC analysis as before gave the results included in Table 4.

References

1 Part 25. T. Lanez and P. L. Pauson, *J. Chem. Soc., Perkin Trans. 1,* 1990, 2437.

2 K. Shibata, Y. Saito, M. Matsui and Y. Takase, *Bull. Chem. Soc. Jpn.,* 1984, **57**, 3349.

3 T. Sato, S. Shimada and K. Hata, *Bull. Chem. Soc. Jpn.,* 1969, **42**, 2731.

4 G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.,* 1955, 367.

5 A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR,* 1954, **97**, 459; A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *Dokl. Akad. Nauk SSSR,* 1954, **99**, 539; A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, *Dokl. Akad. Nauk SSSR,* 1955, **102**, 535.

6 M. Rosenblum, W. G. Howells, A. K. Banerjee and C. Bennett, *J. Am. Chem. Soc.,* 1962, **84**, 2726.

7 R. Huisgen and R. Grashey, *Liebigs Ann. Chem.*, 1957, **607**, 46.
8 R. Bolton, B. N. Dailly, K. Hirakubo, K. H. Lee and G. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1109.
9 J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1954, 3352.
10 P. L. Pauson, J. Šraga and Š. Toma, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1233.
11 J. McDonald Blair, D. Bryce-Smith and W. B. Pengilly, *J. Chem. Soc.*, 1959, 3174.
12 J. K. Hambling, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1962, 487.
13 G. Vernin, R. Jauffred, C. Ricard, H. J. M. Dou and J. Metzger, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1145.
14 R. Ito, T. Migita, N. Morikawa and O. Simamura, *Tetrahedron*, 1965, **21**, 955.
15 T. Migita, N. Morikawa and O. Simamura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 980; R. Îto, T. Migita, N. Morikawa, M. Okuni and O. Simamura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 985.
16 R. L. Dannley and E. C. Gregg, *J. Am. Chem. Soc.*, 1954, **76**, 1463.
17 D. H. Hey, *Tetrahedron Suppl. No. 3*, 1959, 209.
18 A. N. Nesmeyanov, E. G. Perevalova and O. A. Nesmeyanova, *Izv. Akad. Nauk SSSR, Otdl. Khim. Nauk*, 1962, 47.
19 W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn and A. P. Sanders, *J. Am. Chem. Soc.*, 1964, **86**, 1376.
20 H. Shechter and J. F. Helling, *J. Org. Chem.*, 1961, **26**, 1034.
21 M. D. Rausch, *J. Org. Chem.*, 1961, **26**, 1802.
22 R. W. Fish and M. Rosenblum, *J. Org. Chem.*, 1965, **30**, 1253.