

Further Studies on the Photolysis of Ferrocenyl Ethers in Methanol

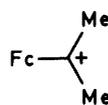
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The photolysis of several ferrocenyl ethers in methanol yields products formed from α -ferrocenyl free radicals and α -ferrocenyl carbocations. The influence of adventitious acid on the reaction has been studied and the conditions for the optimisation of the radical reaction have been established. Possible mechanisms for the reaction are discussed.

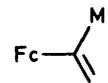
OUR previous study on the photolysis of ferrocenyl olefins¹ in methanol or ethanol identified two processes, namely the addition of alcohol to the olefin by an ionic process, and the secondary photolysis of the ethers produced by the addition. The formation of ferrocenyl alkanes and diferrocenyl ethanes in this latter reaction was interpreted in terms of α -ferrocenyl free radicals and was especially interesting since there are few reports in the literature of such intermediates produced photochemically. Ferrocenyl free radicals have been prepared by several ground-state routes such as the treatment of chloromethylferrocene with lithium² or the reduction of quaternary ammonium methyl ferrocene salts with sodium amalgam.³ Another approach has utilised electron transfer to ferrocenyl carbocations as in the synthesis reported by us⁴ of 2,3-diferrocenyl-2,3-dimethylbutane from 2-ferrocenylpropene in Zn-CH₃-CO₂H or the work of Cais *et al.*⁵ who developed this technique for the synthesis of symmetrical 1,2-diferrocenylethanes.

It was clear from our study¹ that irradiation of the ferrocenyl ethers could produce an excited state which might result in homolysis or heterolysis of the O-C bond. Some evidence for heterolysis and the formation of ion (1) was obtained by the isolation of 2-ferrocenylpropene (2), from the irradiation of the ethers (3), (4), and (5) in alcohol. In these experiments unchanged ferrocenyl ether made up the principal part of the recovered material. It seemed obvious that if the ion (1) was indeed produced by photo-induced heterolysis of the ether then such an ion could equally well be trapped by solvent but this process would remain undetected when

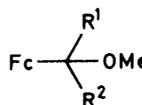
irradiating, for example, an ethyl ether in ethanol. However the isolation of the methyl ether (3) (31%) from the irradiation of the ethyl ether (5) in methanol clearly indicates that an exchange process does occur. In common with previous experiments the olefin (2), the propane (6), and the butane (7) were also isolated, the yields of which are shown in Table 1 (entry 1). This



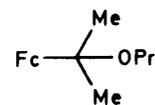
(1) Fc = C₅H₅FeC₅H₄



(2)

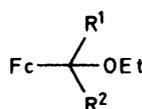


(3) R¹ = R² = Me

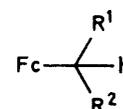


(4)

- (22) R¹ = R² = H
 (23) R¹ = Me, R² = H
 (24) R¹ = Ph, R² = H
 (25) R¹ = Ph, R² = Me
 (26) R¹ = R² = Ph



(5) R¹ = R² = Me



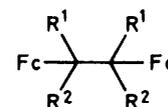
(6) R¹ = R² = Me

TABLE 1
 Influence on product formation of the use of deoxygenated nitrogen and added base on the photolysis of the ferrocenyl ether (5) (entries 1-3) and 2-ferrocenylpropene (2) (entries 4 and 5)

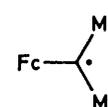
Reaction conditions	Products (%) ^a				
	(6)	(7)	(2)	(3)	(5)
1; MeOH; deaerated with N ₂	4	1	4	31	33 ^b
2; MeOH; deaerated with O ₂ -free N ₂	20	3	2	56	15 ^b
3; MeOH; deaerated with O ₂ -free N ₂ ; Na ₂ CO ₃	35	10		39	^c
4; EtOH; deaerated with N ₂	7	4	16		40
5; MeOH; deaerated with O ₂ -free N ₂ ; Na ₂ CO ₃	21	9		31	

^a Each photolysis yielded some 2-ferrocenylpropan-2-ol. This is not a photo-product but is formed from the ether during chromatography. ^b Recovered starting material. ^c Trace.

- (9) R¹ = R² = H
 (10) R¹ = Me, R² = H
 (11) R¹ = Ph, R² = H
 (12) R¹ = Ph, R² = Me
 (13) R¹ = R² = Ph



(7) R¹ = R² = Me



(8)

- (19) R¹ = R² = H
 (20) R¹ = Me, R² = H
 (21) R¹ = Ph, R² = H

Table (entries 2 and 3) also shows the results from two further experiments where deoxygenated nitrogen was used to deaerate the solution prior to photolysis and sodium carbonate was added as a scavenger of acid. The need for such caution was prompted by two points: (i) the thought that an acid-catalysed ground-state process might be involved in the ether exchange, and (ii) the reports of Cristol *et al.*⁶ and of Roussi and Beugelmans⁷ who reported difficulties experienced due to oxidation of the alcohol to acid, when methanol solutions were irradiated under unpurified nitrogen.

The results (Table 1, entries 1–3) obtained clearly show that while adventitious acid might have had some effect on the ether exchange reaction the greater part of the process is truly photochemical. Table 1 (entries 4 and 5) also show that the irradiation of 2-ferrocenylpropene is little affected by the presence or absence of acid. The most important result from these experiments with the ether (5) was the greatly enhanced yield (from 5 to 45% total) of the products (6) and (7). These products arise from the α -ferrocenyl free radical (8) produced by homolysis of the ether C–O bond.

Our initial objective of obtaining a photochemical source of α -ferrocenyl free radicals was achieved. It was clear that substitution around the radical site could profoundly affect the efficiency of the homolysis process. Thus we investigated the influence such substitution exerted on the partition of the reaction path between homolysis and heterolysis of the ether C–O bond. For this work we required a series of ferrocenyl ethers [the novel ethers synthesised in this work are (11)–(13) and (26)] which were readily prepared by conversion of the appropriate ferrocenyl alcohol in ethanol or methanol with silica gel. This synthetic route is extremely mild and affords high yields of products with little or no decomposition. The method employed by us¹ is a modification of an earlier approach reported by Nesmeyanov *et al.*⁸ The route utilises the mild acidity of the silica gel to produce the ferrocenyl carbocation which is solvated by the appropriate alcohol.

The ethers were irradiated under the standard conditions and the mixture of products obtained was readily separated by column chromatography. The products from the irradiations (Table 2) were readily identified by n.m.r. spectroscopy and/or comparison with authentic material. The results show that increased substitution

at the radical site increases the yield of radical products. This change parallels the expected increase in the stability of the free radicals with increasing substitution. In this respect Nesmeyanov *et al.*³ have reported that a ferrocenyl is slightly less effective than a phenyl group in stabilising a radical. The product of hydrogen abstraction is formed in much greater yield than that of dimerisation since the free radical is formed in a solvent cage and it is therefore more likely to collide with solvent at the concentrations (*ca.* 2×10^{-2} M) used than with an identical free radical. However, as the radical stability is enhanced so it is to be expected that the yield of dimers would increase. This is the case with radicals (8; R¹ = H, R² = Ph) and (8; R¹ = R² = Me) where the yields of dimeric product are 6 and 10%, respectively. When bulkier substituents surround the radical site, as in (8; R¹ = Ph, R² = Me) and (8; R¹ = R² = Ph), no dimeric products are produced and the alkane, produced by hydrogen abstraction from solvent, was the only radical product isolated. Such behaviour is in line with the reactivity of the triphenylmethyl radical which, as a result of bulky substituents, does not undergo frontal dimerisation,⁹ and it is to be expected that hydrogen abstraction is to be preferred.

Table 2 also shows that the photochemical ether exchange process discussed earlier occurs with all the ethers studied.

This study qualitatively shows the scope of the photochemical fission of ferrocenyl ethers. As suggested earlier in this work it seemed a reasonable postulate that photoexcitation affords an excited state which partitions itself into two reaction paths. A summary of this proposal is shown in the Scheme 1. As yet we have not obtained any information concerning the nature of the excited state. However the elegant work of Heaney and Logan¹⁰ has shown that photoexcitation at 254 nm of ferrocenyl-substituted carboxylic acids yields an excited state with a lifetime corresponding to a triplet state. Indeed this triplet in their study¹⁰ is prone to undergo electron transfer from the iron to a suitable acceptor. If a triplet state is involved in the ether photolysis studied by us, and electron transfer follows the excitation, then fission of the C–O bond could arise as shown in Scheme 2. The intermediates (i) and (ii) produced by this path would account for the ionic and free radical products encountered in the photolyses. Indeed the intermediate

TABLE 2
Products [%] from the irradiation of ferrocenyl ethers in methanol^a

Ether	Recovered starting material	Ferrocenylalkane	Diferrocenyethane	Exchange product	Other ^b
(9)	(9) [60]	(14) [14]	(19) [1.6]	(22) [12%]	
(10)	(10) [34]	(15) [15]	(20) [2]	(23) [24%]	
(11)		(16) [29]	(21) [6]	(24) [42%]	
(5)		(6) [35]	(7) [10%]	(3) [21%]	
(12)	(12) [5]	(17) [34]		(25) [41%]	[6] ^c
(13)		(18) [70]		(26) [12%]	

^a Irradiations carried out under oxygen-free nitrogen with Na₂CO₃ added as an acid scavenger. In all the experiments some decomposition was observed. ^b The photolysis of ethers (9)–(11) and (5) also yielded small amounts of the corresponding ferrocenyl alcohol. These are not photo-products but are formed from the ether by exchange during chromatography. ^c 1-Ferrocenyl-1-phenylethylene.

(i) has a precedent in the literature and has been proposed by Rinehart and his co-workers^{11a} to account for the formation of 1,2-diferrocenylethane from the reaction of 1-ferrocenylmethanol in concentrated sulphuric acid, and by us^{11b} in the reduction of 1,3-diferrocenylpropenes in the same medium. Cais *et al.*¹² have also implicated this intermediate (i) in their study of the trapping of the ferrocenyl carbocation by nitrobenzene. However we have not, so far, collected any data from our work which implicate an electron transfer and such proposals must remain purely speculative.

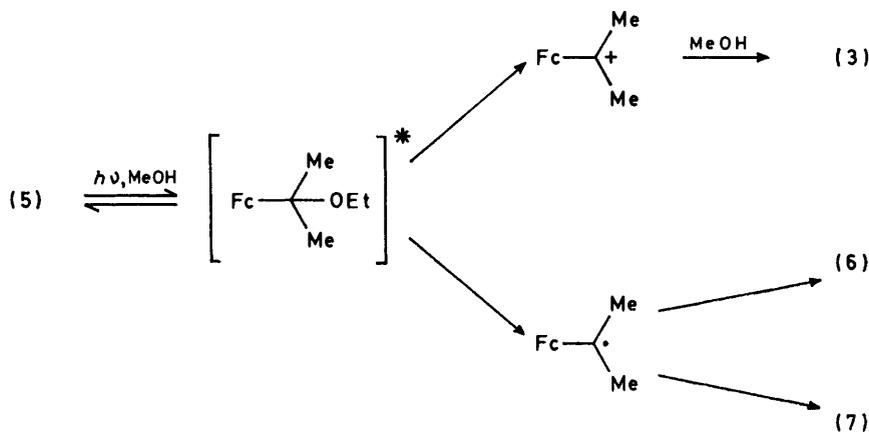
pane^{1,2} and 2-ferrocenylpropan-2-ol,² in trace quantities, were eluted by ether.

(b) *Using oxygen-free N₂.* The ether (5) (1.0 g) was photolysed for 10.5 h to yield the same products as in (a).

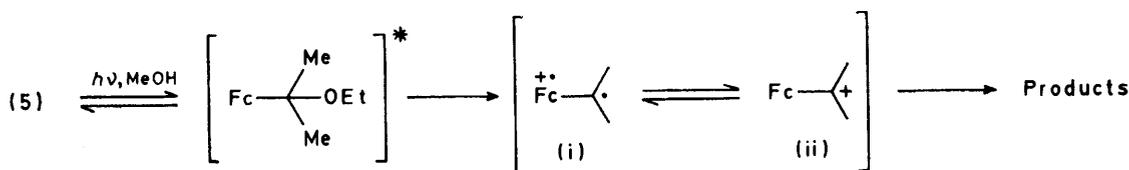
(c) *Using oxygen-free N₂-Na₂CO₃.* The ether (5) (1.01 g) was stirred and photolysed for 16 h in methanol with Na₂CO₃ (1.0 g, anhydrous).

Photolysis of 2-Ferrocenylpropene.—The olefin (2) (1.52 g) and Na₂CO₃ (2.0 g, anhydrous) in a stirred solution of methanol (200 ml) was photolysed through quartz for 16 h.

Ferrocenyl Alcohols.—1-Ferrocenylethanol and ferrocenylphenylmethanol were prepared by reduction with



SCHEME 1



SCHEME 2

EXPERIMENTAL

Photoreactions were performed on solutions in methanol (200 ml) in a water-cooled immersion-well apparatus using a Hanovia 450-W medium-pressure mercury-arc lamp and a quartz well. A slow purge of nitrogen, in most cases deoxygenated by passing the gas through two Dreschel bottles of vanadous sulphate solution,¹³ was used to deoxygenate the solution prior to (for 1 h) and during the photolysis. The photoreactions were worked up by removal of the solvent under reduced pressure followed by column chromatography. Light petroleum used was of 60–80° boiling range. The alumina for chromatography was Spence Grade H, and silica gel was Hopkin and Williams' Silica for Chromatography. N.m.r. spectra were recorded on a Perkin-Elmer R10 60 MHz spectrometer with tetramethylsilane as internal standard.

2-Ferrocenylpropene was prepared from acetylferrocene and methylene triphenylphosphorane.¹⁴

Photolysis of 2-Ethoxy-2-ferrocenylpropane (5).—(a) *Using unpurified N₂.*—2-Ethoxy-2-ferrocenylpropane (5) (1.06 g) in methanol (200 ml) was irradiated for 16 h. 2-Ferrocenylpropane,^{1,2} 2-ferrocenylpropene, 2,3-diferrocenyl-2,3-dimethylbutane, m.p. 215–216° (lit.⁴ 215–216°), and 2-ethoxy-2-ferrocenylpropane¹ were eluted with light petroleum–benzene (1:1). 2-Ferrocenyl-2-methoxypro-

pane^{1,2} and 2-ferrocenylpropan-2-ol,² in trace quantities, were eluted by ether.

1-Ferrocenyl-1-phenylethanol was prepared by the slow addition of methyl-lithium (25 ml; 1.0M) to a stirred ethereal solution (150 ml) of benzoylferrocene (4.8 g). After conventional work-up, chromatography of the residue using ether yielded 1-ferrocenyl-1-phenylethanol (4.3 g, 84%) as yellow-orange crystals, m.p. 109–111° (from light petroleum–benzene) (lit.,¹⁵ 110–111°).

Ferrocenyldiphenylmethanol was prepared by the slow addition of benzoylferrocene (4.0 g) in ether (100 ml, anhydrous) to phenylmagnesium bromide [prepared from bromobenzene (3.2 ml) and magnesium (1 g) in ether (15 ml)]. Conventional work-up and chromatography with ether as eluant yielded ferrocenyldiphenylmethanol (3.5 g, 68%) as yellow needles, m.p. 134–136° (from light petroleum–benzene) (lit.,¹⁶ 133–136°).

Ferrocenyl Ethers.—The ferrocenyl ethers required as reactants or for proof of structures were prepared by the following general method.

The ferrocenyl alcohol (0.02 mol) was dissolved in the appropriate alcohol (100 ml). Silica gel (2.0 g) was added and the mixture was allowed to stand at ambient temperature for 24 h. The reaction was quenched in sodium hydrogencarbonate solution and the organic material was

extracted into ether. The ether extracts were washed with water, dried (MgSO_4), filtered, and evaporated to dryness. The residue was chromatographed on alumina with light petroleum-benzene (1:1) as eluant. The following ethers were obtained: *ethoxyferrocenylphenylmethane* (11) as orange-yellow crystals, m.p. 54–55° (from pentane), $\delta(\text{CDCl}_3)$ 1.23 (3 H, t), 3.43 (2 H, q), 4.01 (9 H, s), 5.02 (1 H, s), and 7.31 (5 H, s) (Found: C, 71.5; H, 6.55. $\text{C}_{19}\text{H}_{20}\text{OFe}$ requires C, 71.45; H, 6.25%); *1-ethoxy-1-ferrocenyl-1-phenylethane* (12) as orange-yellow crystals, m.p. 68–69.5° (from pentane), $\delta(\text{CDCl}_3)$ 1.14 (3 H, t), 1.80 (3 H, s), 3.19 (2 H, q), 4.00br (9 H, s), and 7.52–7.06 (5 H, m) (Found: C, 72.15; H, 6.7. $\text{C}_{20}\text{H}_{22}\text{OFe}$ requires C, 72.1; H, 6.6%); *ethoxyferrocenyldiphenylmethane* (13) as orange crystals, m.p. 93.5–95.0° (from pentane), $\delta(\text{CDCl}_3)$ 1.17 (3 H, t), 3.27 (2 H, q), 3.91br (s), 4.04br (9 H, s), and 7.23br (10 H, s) (Found: C, 75.9; H, 6.05. $\text{C}_{25}\text{H}_{24}\text{OFe}$ requires C, 75.75; H, 6.05%); *ferrocenylmethoxydiphenylmethane* (26) as orange needles, m.p. 99–100° (from pentane), $\delta(\text{CDCl}_3)$ 3.20 (3 H, s), 4.04br (s), 4.17br (9 H, s) and 7.34br (10 H, s) (Found: C, 75.5; H, 6.0. $\text{C}_{24}\text{H}_{22}\text{OFe}$ requires C, 75.3; H, 5.8%).

Photolysis of 1-Ethoxy-1-ferrocenylmethane (9).—The ether (1.02 g) ² and Na_2CO_3 (1.1 g, anhydrous) in a stirred solution of methanol (200 ml) were photolysed through quartz for 15 h. Chromatography of the oily residue afforded ferrocenylmethane,² 1,2-diferrocenylethane as yellow crystals, m.p. 202–203° (from pentane) (lit.,¹⁷ 200–200.5), and ethoxyferrocenylmethane, all eluted with light petroleum-benzene (1:1); ferrocenylmethoxymethane, $\delta(\text{CDCl}_3)$ 3.25 (3 H, s), 4.05br (s), 4.24br (11 H, s), eluted with benzene-ether (1:1); and ferrocenylmethanol as yellow needles, m.p. 80–81° (from light petroleum-benzene) (lit.,¹⁸ 80–81°), eluted with ether.

Photolysis of 1-Ethoxy-1-ferrocenylethane (10).—The ether ¹ (1.04 g) and Na_2CO_3 (1.2 g) were stirred in methanol and photolysed through quartz for 16 h. Chromatography on alumina afforded ferrocenylethane,¹ 2,3-diferrocenylbutane ¹ as a mixture of diastereoisomers, red-orange crystals, m.p. 132–133° and 1-ethoxy-1-ferrocenylethane, all eluted with light petroleum-benzene (1:1); and 1-ferrocenyl-1-methoxyethane and 1-ferrocenylethanol, yellow solid, m.p. 78–79° (lit.,¹⁹ 78–79°), both eluted with ether.

Photolysis of Ethoxyferrocenylphenylmethane (11).—The ether (1.00 g) and Na_2CO_3 (1.2 g, anhydrous) in methanol were photolysed through quartz for 16 h. Chromatography of the oily residue yielded ferrocenylphenylmethane as orange needles, m.p. 76–77° (from pentane) (lit.,²⁰ 75–76°) 1,2-diferrocenyl-1,2-diphenylethane as a mixture of diastereoisomers, yellow crystals, m.p. 209–211° (lit.,²¹ 217–220 and 278–280°), and (ferrocenyl)methoxyphenylmethane as orange crystals, m.p. 114–115° (from pentane) (lit.,²² 113–114°), all eluted with light petroleum-benzene (1:1); and ferrocenylphenylmethanol as yellow crystals, m.p. 81–82° (lit.,²³ 81–82°), eluted with ether.

Photolysis of 1-Ferrocenyl-1-ethoxy-1-phenylethane (12).—The ether (1.03 g) and Na_2CO_3 (1.0 g, anhydrous) in methanol were photolysed through quartz for 13 h. Chromatography of the residue afforded 1-ferrocenyl-1-phenylethane as orange plates, m.p. 43–44° (from pentane) (ref. 24 described this compound as an oil), $\delta(\text{CDCl}_3)$ 1.53 (3 H, d), 3.89 (1 H, q), 3.98br (9 H, s), and (5 H, s) 7.19 (Found: C, 74.6; H, 6.15. $\text{C}_{18}\text{H}_{16}\text{Fe}$ requires C, 74.8; H, 6.25%),

1-ferrocenyl-1-phenylethylene,²⁵ and 1-ethoxy-1-ferrocenyl-1-phenylethane, all eluted with light petroleum-benzene (1:1); and 1-ferrocenyl-1-methoxy-1-phenylethane as orange crystals, m.p. 73–74° (from pentane) $\delta(\text{CDCl}_3)$ 1.80 (3 H, s), 3.02 (3 H, s), 3.94 (9 H, s), and 7.09–7.43 (5 H, m) (Found: C, 71.9; H, 6.35. $\text{C}_{19}\text{H}_{20}\text{OFe}$ requires C, 71.5; H, 6.25%), eluted with ether.

Photolysis of Ethoxyferrocenylphenylmethane (13).—The ether (0.79 g) and Na_2CO_3 (1.2 g, anhydrous) were photolysed through quartz for 15 h. Chromatography of the residue on alumina afforded ferrocenyldiphenylmethane (0.49 g, 69.8%) as orange crystals, m.p. 86–87° (from pentane); $\delta(\text{CDCl}_3)$ 3.89br (s), 4.06 (9 H, m), 5.09 (1 H, s), and 7.19 (10 H, s) (Found: C, 78.25; H, 5.85. $\text{C}_{23}\text{H}_{20}\text{Fe}$ requires C, 78.4; H, 5.7%), and ferrocenylmethoxydiphenylmethane (0.092 g, 12.3%) as orange yellow crystals, m.p. 99–100° (from pentane), both eluted with light petroleum-benzene (7:3). Ethanol eluted an intractable mixture (0.26 g).

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