Photolysis of Ferrocenyl-olefins and -ethers in Alcohols [1]

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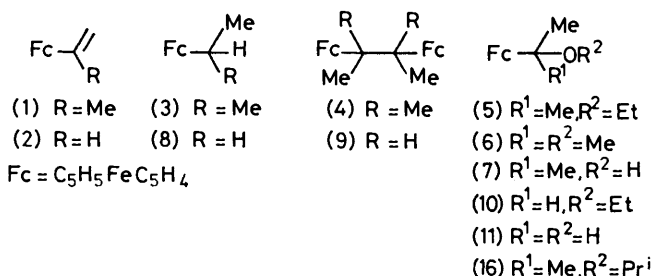
The irradiation of solutions of 2-ferrocenylpropene and ferrocenylethylene in methanol and ethanol has been studied. The primary photochemical process is interpreted as involving ferrocenyl carbocation intermediates which yield ferrocenyl ethers. These ethers are themselves photolabile, yielding 2-ferrocenylpropane and 2,3-diferrocenyl-2,3-dimethylbutane from 2-ferrocenylpropene, and ferrocenylethane and 2,3-diferrocenylbutane from ferrocenylethylene. These latter reactions are thought to involve ferrocenyl free radicals.

THE investigation of the photochemical behaviour of ferrocenyl systems has had sporadic attention over the years, and a review of the area has been published.[2a] The studies reported have dealt with several principal areas: (a) oxidation of the iron atom; [2b] (b) oxidation of the iron atom with subsequent radical addition to the ferrocenyl nucleus; [2c] (c) fission of the ligand–Fe bond; [2d] (d) fission of bonds between the cyclopentadienyl ligand and attached groups to yield σ-ferrocenyl radicals; [2e] and (c) reactions of side-chains attached to the cyclopentadienyl ring.[2f] It is towards the last of these that the present work has been directed.

Previous work in this area has dealt with the reduction of ferrocenyl ketones [3] and with the *trans–cis* isomerisation of 1-ferrocenyl-2-phenylethylene [4] and of 1-ferrocenyl-2-phenanthrenylethylene.[5] In these olefinic examples no evidence was put forward for the formation of products other than geometric isomers. Thus it was in this light that we undertook the study of the irradiation of ferrocenylolefins.

RESULTS AND DISCUSSION

We anticipated that protic solvents would be necessary for clean photoreaction of the olefins 2-ferrocenylpropene (1) and ferrocenylethylene (2). This opinion was re-

(1) R = Me   (3) R = Me   (4) R = Me   (5) R¹ = Me, R² = Et
(2) R = H   (8) R = H   (9) R = H   (6) R¹ = R² = Me
Fc = C₅H₅FeC₅H₄   (7) R¹ = Me, R² = H
                                                (10) R¹ = H, R² = Et
                                                (11) R¹ = R² = H
   (16) R¹ = Me, R² = Prⁱ

inforced by the observed destruction of 2-ferrocenylpropene when it was irradiated (450 W lamp) through quartz in cyclohexane. A much cleaner reaction was observed when the olefin (1) was irradiated in pure, dry ethanol or methanol. Under these conditions four products were produced which were readily separated by column chromatography. The first product eluted was identified as 2-ferrocenylpropane (3) [4% (EtOH), 7% (MeOH)], which was followed by unreacted starting material and then by 2,3-diferrocenyl-2,3-dimethylbutane (4) [4% (EtOH), 1.5% (MeOH)]. This product was readily identified by comparison with an authentic

sample.[6] The main products from the reaction were the ethers 2-ethoxy-2-ferrocenylpropane (5) (65%) in EtOH, and 2-methoxy-2-ferrocenylpropane (6) (26%) in MeOH. The fourth product was 2-ferrocenylpropan-2-ol (7). This alcohol is an artifact of the separation, since it is well known that ferrocenyl ethers can be converted, on prolonged exposure to alumina under conditions of chromatography, into the alcohol.[7] Such a transformation is a further manifestation of the stability of α-ferrocenylcarbocations.[8]

Irradiation of ferrocenylethylene (2) in ethanol under the same conditions as above gave an analogous set of products, *i.e.* ferrocenylethane (8) (4%), unchanged ferrocenylethylene, 2,3-diferrocenylbutane (9) (4%), 1-ethoxy-1-ferrocenylethane (10) (58%), and 1-ferrocenylethanol (11) (9%).

The identity of the products from the irradiation could be readily confirmed from their spectral characteristics. The ferrocenyl ethers, which were required for a further study, were independently synthesised from the ferrocenyl alcohol and the desired alcohol utilising silica gel as the source of acid. This is a very mild route to the ferrocenyl ethers [(5), (6), (10), and (16)] and high yields can be obtained with a minimal amount of decomposition.

The formation of the ethers [(5), (6), and (10)] in the photochemical reactions is best accounted for by an ionic mechanism. Protonation of the excited state of the olefin yields an α-ferrocenyl carbocation which would be readily trapped by solvent to afford the ethers [equation (1)]. There are many examples in the literature of the photochemical addition of protic solvents to cyclic olefins. In these, evidence has been obtained implicating a *trans*-olefin or a twisted state which thermally adds an alcohol or a carboxylic acid.[9] There
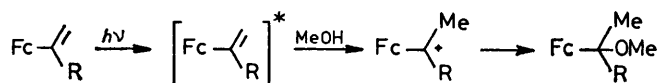

Equation (1)

are fewer examples of additions to simple non-cyclic olefins, although Kropp and his co-workers[10] have suggested the involvement of Rydberg transitions, involving electron expulsion and the formation of a radical cation, in the photolysis of 2,3-dimethylbut-2-ene and related systems. More closely akin to our system is the work of Nozaki and his co-workers [11] and of

Hixson,[12] who have studied the styryl systems (12) and (13) respectively. In these molecules, as in the examples studied by us, no strained olefin can be formed which could result in the thermal addition of solvent. The one feature common to the examples [(1), (2), (12), and (13)] is the presence of an electron-donating aryl group


(12) R = MeO, HO, or NH2   (13)
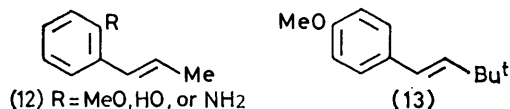
which Hixson[12] has shown to be essential for efficient addition to take place.

In an effort to explain the process Nozaki and his co-workers[11] suggested the involvement of a polar state such as (14). Indeed in the light of current interest in photochemical charge-transfer processes[13] it could be

(14)   (15)
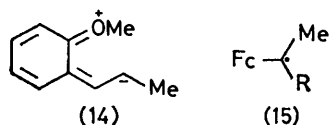
argued that a single electron process rather than electron-pair involvement is more feasible. However, even in our examples where the involvement of the iron atom has been sought, there is no evidence to hand which might clarify the situation.

The cationic path described above does not readily explain the formation of the reduction products (3), (4), (8), and (9). The simplest explanation for their form-ation is via a free radical (15), which could be produced by initial excitation and hydrogen abstraction from solvent. However, the experiment with 2-ferrocenyl-propene in cyclohexane, which only resulted in decom-position, indicates otherwise. Thus an alternative explanation was sought, and attention was turned to the ferrocenyl ethers. The photolability of these com-pounds, under irradiation conditions identical to those used for the ferrocenyl olefins, was readily demonstrated by their separate irradiation. Thus the irradiation of 2-ferrocenyl-2-ethoxypropane (5) in ethanol yielded the same products, 2-ferrocenylpropane and 2,3-diferro-cenyl-2,3-dimethylbutane, as were obtained from the irradiation of 2-ferrocenylpropene in the same solvent. Similar behaviour was observed for the irradiation of 2-ferrocenyl-2-methoxypropane (6) in methanol. Both these experiments also yielded 2-ferrocenylpropene (1) as the main product indicating either loss of hydrogen from radical (15), or more likely loss of a proton from a carbocation intermediate (17), was occurring. This

(17)
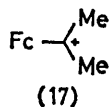
sequence suggests that photoexcitation of the ferrocenyl ethers leads to both homolytic and heterolytic fission of

the C–O bond. The irradiation of 2-ferrocenyl-2-isopropoxypropane in propan-2-ol also exhibited this tendency, producing 2-ferrocenylpropane and 2-ferro-cenylpropene. These reactions are illustrated in equa-tion (2).

In summary, we have demonstrated that irradiation of simple ferrocenylolefins in alcohol results in photo-
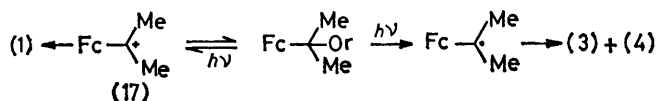
Equation (2)

excitation to a state which is readily protonated by solvent. The resultant carbocation intermediate is trapped as a ferrocenyl ether. The ferrocenyl ethers so produced are also photolabile and undergo either homo-lytic or heterolytic fission. The fate of the free radicals produced by homolysis is either hydrogen abstraction or dimerisation.

EXPERIMENTAL

Photo-reactions were performed in a water-cooled immer-sion-well apparatus using a Hanovia 450 W medium-pressure mercury-arc lamp and a quartz well. A slow purge of nitrogen was used to deoxygenate the reaction mixture prior to photolysis, and was maintained throughout the period of photolysis. Light petroleum used had b.p. 60—80 °C. The alumina was Spence Grade H. Silica gel was Hopkin & Williams 'silica for chromatography'.

Irradiation of 2-Ferrocenylpropene in Ethanol.—2-Ferro-cenylpropene (2.5 g) in dry ethanol (220 ml) was degassed for 1 h by passage of white-spot nitrogen. The degassed solution was then photolysed through quartz for 36 h using a Hanovia medium-pressure 450 W lamp. Excess of solvent was removed under reduced pressure and the oily residue chromatographed on alumina to yield from fraction one (eluant light petroleum), 2-ferrocenylpropane (0.10 g, 4%) as an orange-yellow oil, b.p. (at 0.4 mmHg) 72—73 °C (lit.,[14] b.p. at 0.4 mmHg 73—74 °C); $\nu_{max.}$ 3 000—2 850 (alkyl), 1 100, 1 000, and 815 cm^{-1} (Fc); δ(CDCl$_3$) 1.21 (6 H, d), 2.39—2.86 (1 H, m), and 4.12 and 4.17 (9 H, 2 s): from fraction two (eluant petrol), 2-ferrocenylpropene (0.32 g, 13%); from fraction three, 2,3-diferrocenyl-2,3-dimethyl-butane (0.15 g, 4%) as yellow crystals (from pentane), m.p. 215—216 °C (lit.,[6] m.p. 215—216 °C); $\nu_{max.}$ (Nujol 2 900) (alkyl), 820—800, 920, and 1 100 cm^{-1} (Fc); δ(CDCl$_3$) 1.16 (12 H, s), and 3.74, 3.97, and 4.01 (18 H); from fraction four [eluant petrol–benzene (5 : 1)] 2-ethoxy-2-ferrocenylpropane (1.82 g, 65%) as orange crystals, m.p. 67—68.5 °C; and from fraction five (eluant ether) 2-ferro-cenylpropan-2-ol (0.060 g, 2%).

Irradiation of 2-Ferrocenylpropene in Methanol.—2-Ferrocenylpropene (2.5 g) in methanol (200 ml) was degassed for 1 h and photolysed for 22 h using the conditions employed above. Excess of methanol was removed and the oily residue subjected to alumina chromatography. Frac-tion one (petrol) yielded 2-ferrocenylpropane (0.167 g, 7%) as an orange-yellow oil; fraction two (from petrol) yielded 2-ferrocenylpropene (0.730 g, 29%); fraction three [eluant petrol–benzene (9 : 1)] yielded 2,3-diferrocenyl-2,3-dimethyl-butane (0.071 g, 1.5%) as yellow crystals (from pentane), m.p. 215—216 °C; and from fraction four [eluant benzene–ether

(50 : 1)] yielded 2-ferrocenyl-2-methoxypropane (0.75 g, 26%).

Irradiation of Ferrocenylethylene in Ethanol.—Ferrocenylethylene (2.5 g) in ethanol (220 ml) was degassed for 1 h and photolysed under the conditions employed above for 69 h. Excess of solvent was removed and the oily residue chromatographed on alumina to yield from fraction one (eluant petrol), ferrocenylethane (0.093 g, 4%) as a red oily liquid, b.p. at 0.2 mmHg 76—78 °C (lit.,[15] b.p. at 0.2 mmHg, 74—76 °C); $\delta(CDCl_3)$ 1.11 (3 H, t, J 7 Hz), 2.22 (2 H, q, J 7 Hz), and 3.89 (9 H, s); from fraction two (eluant petrol), ferrocenylethylene (0.35 g, 14%); from fraction three [eluant petrol–benzene (9 : 1)], 2,3-diferrocenylbutane (0.184 g, 4%) as a mixture of diastereoisomers, orange-yellow crystals (from pentane), m.p. 132—133 °C (lit.,[16] m.p. 115—116 or 144—145 °C); $\nu_{max.}$ (Nujol) 3 000—2 900 (alkyl), 1 100, 1 000, and 820 cm^{-1} (Fc); $\delta(CDCl_3)$ 1.01, 1.12 (6 H, 2 overlapping d), 2.74—2.25 (2 H, m), and 3.74, 3.95, and 3.99 (18 H) (Found: C, 67.85; H, 5.90. $C_{24}H_{26}Fe_2$ requires C, 67.64; H, 6.10%); from fraction four (eluant benzene), 1-ethoxy-1-ferrocenylethane (1.78 g, 58%); and from fraction five (eluant ether), 1-ferrocenylethanol (0.24, 9%) as yellow needles (from pentane), m.p. 76—78 °C (lit.,[17] m.p. 78—79 °C).

2-Ethoxy-2-ferrocenylpropane (5).—2-Ferrocenylpropan-2-ol (5.0 g) in methanol (100 ml) and silica gel (2.0 g) were stirred together at room temperature for 24 h. The reaction was quenched with saturated NaHCO$_3$ solution and extracted into ether. The ether extracts were washed with water (2 × 100 ml), dried (MgSO$_4$), filtered, and excess of solvent removed. The residue was chromatographed on alumina to yield from fraction one (eluant petrol), 2-ferrocenylpropene (0.72 g, 14%); from fraction two [eluant petrol–benzene (1 : 1)], 2-ethoxy-2-ferrocenylpropane (4.0 g, 78%) as orange-yellow needles (from pentane), m.p. 67—68.5 °C; $\nu_{max.}$ (Nujol) 3 000—2 850 (alkyl); 820, 1 000, and 1 110 (Fc); and 1 064, 1 015, 1 152, and 1 265 cm^{-1} (OMe); $\delta(CDCl_3)$ 1.00 (3 H, t), 1.54 (6 H, s), 3.11 (2 H, q), and 4.08 and 4.10 (9 H, singlets) (Found: C, 65.9; H, 7.15. $C_{15}H_{20}FeO$ requires C, 66.16; H, 7.41%); and from fraction three (eluant ether), 2-ferrocenylpropan-2-ol (0.4 g, 12%).

2-Ferrocenyl-2-methoxypropane (6).—In the same manner as above, 2-ferrocenyl-2-methoxypropane was obtained as a dark red oil which solidified at 0 °C and was successfully recrystallised from pentane, m.p. 28—30 °C (lit.,[16] m.p. 25—26 °C); $\nu_{max.}$ 3 000—2 950 (alkyl); 1 100, 1 000, and 815 (Fc); 1 160, 1 150, and 1 030 cm^{-1} (OMe): $\delta(CDCl_3)$ 1.39 (6 H, s), 2.94 (3 H, s), and 4.17 (9 H, br s).

1-Ferrocenyl-1-ethoxyethane (10).—Using the same procedure and scale as in the above experiment, 1-ferrocenyl-1-ethoxyethane was obtained as a red viscous oil, b.p. at 2 mmHg 120 °C; $\nu_{max.}$ 3 010, 2 960, and 2 972 (alkyl); 815(br), 1 000, and 1 110 (Fc); 1 020, 1 100, 1 080, and 1 230 cm^{-1} (Me); $\delta(CDCl_3)$ 1.11 (3 H, t), 1.45 (3 H, d), 3.38 (2 H, q), and 4.05 and 4.17 (10 H) (Found: C, 64.9; H, 7.0. $C_{14}H_{18}FeO$ requires C, 65.14; H, 6.98%).

2-Ferrocenyl-2-isopropoxypropane (16).—Using the same procedure and scale as above, 2-ferrocenyl-2-isopropoxypropane was obtained as orange crystals (from pentane), m.p. 68.5—69.5 °C (from pentane); $\nu_{max.}$ (Nujol) 3 000—2 900 (alkyl); 820, 1 000, and 1 110 (Fc); 1 375, and 1 360 cm^{-1} (OPr); $\delta(CDCl_3)$ 0.84 (6 H, d), 1.53 (6 H, s), 3.52 (1 H, m), and 4.07 (9 H, br s) (Found: C, 67.35; H, 7.60. $C_{16}H_{22}FeO$ requires C, 67.16; H, 7.69%).

Irradiation of 2-Ethoxy-2-ferrocenylpropane in Ethanol.—2-Ethoxy-2-ferrocenylpropane (2.04 g) in ethanol (200 ml) was degassed for 1 h and then photolysed for 36 h using the conditions employed above. Excess of solvent was removed and the red oily residue chromatographed on alumina to afford from fraction one (eluant petrol), 2-ferrocenylpropane (0.17 g, 7%) as an orange-yellow oil; $\delta(CDCl_3)$ 1.14 (6 H, d, J 7 Hz), 2.53 (1 H, septet, J 7 Hz), and 3.88 (9 H, br s): from fraction two [eluant petrol–benzene (9 : 1)] 2-ferrocenylpropene (0.40 g, 16%) as orange crystals; from fraction three [eluant petrol–benzene (9 : 1)], 2,3-diferrocenyl-2,3-dimethylbutane (0.11 g, 4%) as yellow crystals, m.p. 215—216 °C; from fraction four [eluant benzene–ether (1 : 1)], 2-ethoxy-2-ferrocenylpropane (0.81 g, 40%) as orange-yellow crystals, m.p. 67—68.5 °C; and from fraction five (eluant ether), 2-ferrocenylpropan-2-ol (0.63 g, 27%).

Irradiation of 2-Ferrocenyl-2-methoxypropane in Methanol.—2-Ferrocenyl-2-methoxypropane (2.0 g) in methanol (200 ml) was degassed by passage of N$_2$ for 1 h and then photolysed under the conditions employed previously for 36 h. Removal of excess of solvent and chromatography on alumina afforded from fraction one [eluant petrol–benzene (9 : 1)], 2-ferrocenylpropane (0.21 g, 9%) as an orange-yellow oil; from fraction two [eluant petrol–benzene (5 : 1)], 2-ferrocenylpropene (0.35 g, 16%); from fraction three [eluant petrol–benzene (1 : 1)], 2,3-diferrocenyl-2,3-dimethylbutane (0.12 g, 7%), m.p. 215—216 °C; from fraction four (eluant ether), 2-methoxy-2-ferrocenylpropane (0.74 g, 37%) as a red mobile oil; and from fraction five (eluant ether), 2-ferrocenylpropan-2-ol (0.43 g, 10%).

Irradiation of 2-Ferrocenyl-2-isopropoxypropane in Propan-2-ol.—2-Ferrocenyl-2-isopropoxypropane (1.51 g) in propan-2-ol (220 ml) was degassed by passage of N$_2$ for 1 h and then photolysed for 48 h under the conditions employed above. Excess of solvent was removed and the residue chromatographed on alumina to yield from fraction one [eluant petrol–benzene (5 : 1)], 2-ferrocenylpropane (0.069 g, 6%) as a yellow-orange oil; from fraction two [eluant petrol–benzene (5 : 1)], 2-ferrocenylpropene (0.36 g, 30%); from fraction three (eluant ether), 2-ferrocenyl-2-isopropoxypropane (0.50 g, 33%); and from fraction four (eluant ether), 2-ferrocenylpropan-2-ol (0.31 g, 24%).

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