# Photochemistry of 3-Ferrocenyl-1-p-methoxyphenylprop-1-ene

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The u.v. irradiation of 3-ferrocenyl-1-p-methoxyphenylprop-1-ene in methanol affords 3-ferrocenyl-p-methoxy-phenylpropane (6), 3-ferrocenyl-1-methoxy-1-p-methoxyphenylpropane (10a), and 3-ferrocenyl-3-methoxy-1-p-methoxyphenylpropane (7a). The synthesis and photolysis of 3,3-dideuterio-3-ferrocenyl-1-p-methoxy-phenylpropane has also been studied and from this it has been shown that the ether (10) is formed by photo-addition of methanol and ether (7) which involves a 1,3-hydride transfer reaction. The hydrocarbon (6) is formed by photolysis of either ether (7) or (10).

OUR previous studies of the photochemistry of simple ferrocenyl olefins (1) [1] identified an ionic photoaddition reaction which yielded the ferrocenyl ethers (2). These ethers were also photolabile [2] and could either undergo
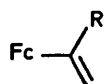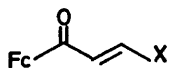

(1) Fc = $C_5H_5FeC_5H_4$

(2)

(3)

(4)

(5)

(6)

X = C_6H_4OMe —p
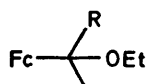
homolysis or heterolysis of the ether O–C bond. In view of our results with these compounds it was of interest to study a system where the double bond was no longer in conjugation with the ferrocenyl group. The molecule chosen for this study was the .propene (3) an example of a 1,3-diarylpropene, a group of compounds (4) whose photochemistry has been well studied.[3] The principal reaction of these species involves cyclisation to cyclopropane derivatives via a di-π-methane path;[4] this can be brought about with both electron-withdrawing and electron-accepting groups. However the incorporation of a ferrocenyl group has not previously been studied.

The olefin (3) was readily synthesised [5] by the mixed hydride reduction of the chalcone analogue (5) and shown to be pure by n.m.r. and t.l.c. analysis. Watts et al.[5] also report the absence of the isomeric olefin from this reduction in contrast to the behaviour of chalcones under similar conditions.[6] The olefin (3) was irradiated in methanol under an atmosphere of oxygen-free nitrogen. The products of the reaction were readily separated, by

conventional column chromatography, into a hydro-carbon (6) (1%), recovered starting material (3) (43%), and two methoxy-ether products (A) (38.5%) and (B) (14%). Although the n.m.r. spectra of the two ethers (A) and (B) were in accord with their identification as 1-methoxy- and 3-methoxy-3-ferrocenyl-1-p-methoxy-phenylpropanes, it was difficult to assign which was which without the help of an unambiguous synthesis.

The synthesis of 3-ferrocenyl-3-methoxy-1-p-methoxy-phenylpropane (7a) was readily carried out in a three-step synthesis involving Friedel–Crafts acylation of ferrocene with 3-p-methoxyphenylpropionyl chloride, hydride reduction of the resultant ketone (8) to the alcohol (9) and conversion of the alcohol in $MeOH–HCO_2H$ into the ether (7a). Comparison of this compound with the photoethers readily identified the minor product (B) with (7a).

As a result of the above assignment it was assumed that the other photoether (A) had the structure (10). To verify this we synthesised this ether utilising the re-activity of the alcohol (11a) prepared by anhydride reduction of (5). Treatment of this alcohol with MeOH–silica gel at room temperature converted it into a 60 : 40 mixture of the two ethers (11b) and (12). This ether mixture (64 : 36) had previously been obtained by Watts
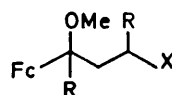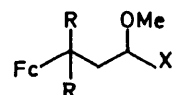

(7) a, R = H
    b, R = D
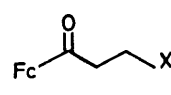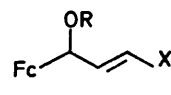
(8)
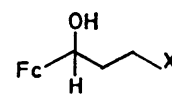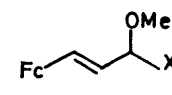
(9)

(10) a, R = H
     b, R = D

(11) a, R = H
     b, R = Me

(12)

X = C_6H_4OMe —p

et al.[5] following the formation of the cation (13) from the olefin (3) by hydride abstraction and quenching by methoxide. It is most likely that reaction of the alcohol (11a) with MeOH–silica gel also involves the ion

(13). The mixture of ethers was catalytically reduced and the resultant reaction mixture was separated by column chromatography. This yielded the alkane (6), and the two ethers (10a), identical with the photoether (A) and (7a) identical with photoether (B). The formation of the alkane (6) in this reaction presumably occurs by hydrogenolysis of either ether, (7) or (10), by analogy with the well documented reactivity of benzyl ethers towards hydrogenolysis.[7]

By analogy with our previous studies [1,2] where α-ferrocenyl ethers were shown to be photolabile, it seemed likely that the hydrocarbon (6) was formed by secondary photolysis of the ferrocenyl ether (7a). This is indeed the case and it was shown that the ether (10a) is also photolabile and yields (6) on independent photolysis. The photolability of benzyl systems has been known for some time, commencing with the photosolvolyses of benzyl esters described by Zimmerman.[8] In some examples, as in the photolysis of benzyl chloride [9] or 3,5-dimethoxybenzyl acetate,[10] benzyl free-radicals are produced. In none of the examples is the fission of an O–C ether linkage involved. Indeed it is readily established, under the conditions used for the irradiation of (7) and (10), that simple benzyl ethers [e.g. methoxy-(phenyl)methane] do not undergo homolysis to a detectable extent. It is not inconceivable, therefore, that the ferrocenyl group assists the C–O homolysis. The exact nature of the involvement of the ferrocene is not clear, although the possibility of discrete electron transfer cannot be discounted.[2]

The rationalisation of a reasonable mechanistic path to the two photoethers (7) and (10) proved to be more difficult. Several routes (Scheme) appeared feasible and it was necessary to try to simplify this situation. The most logical method to achieve this goal was by the use of the labelled compound (14) which was readily synthesised by lithium aluminium deuteride–AlCl₃ reduction of (5).


(13)　　　(14)　　　(16)

X = C₆H₄OMe–p
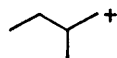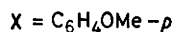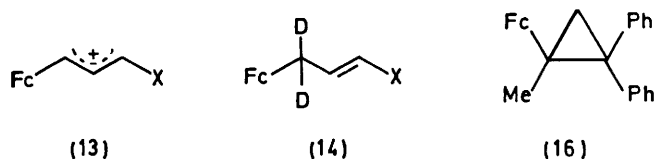
(18)
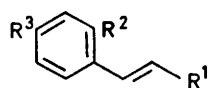
(19) a, R¹= Me : R³= H : R²= OMe, OH, or NH₂
　　 b, R¹= Buᵗ : R²= H . R³= OMe

The irradiation of this olefin (14) and the separation of products was carried out in a similar fashion to that for the olefin (3). The two ethers were readily identified by their n.m.r. spectra (Figure c,d) which were compared

with the spectra of the non-deuteriated ethers (Figure a,b). The most distinctive feature of these spectra is the change in the patterns and integrated areas of the peaks in the δ 1.5—2.8 region. The deuteriated ether (10b) shows the absence of the multiplet at ca. 2.30 for the protons on C-3 adjacent to the ferrocenyl group. The multiplet at δ ca. 1.9, which owes its complexity to the diastereotopic nature of the protons, still integrates for two hydrogens, indicating that there has been no incorporation of deuterium at C-2. These facts prove that the addition of solvent to the olefin (14) has followed route b (Scheme) yielding the ion (15) which is trapped by solvent. The non-appearance of deuterium at C-2 eliminates any involvement of a cyclopropane inter-

X = C₆H₄OMe –p
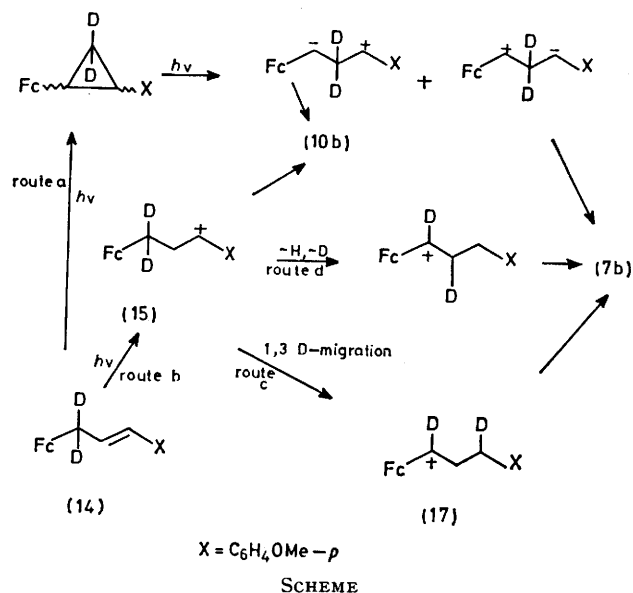
SCHEME

mediate as suggested by route a (Scheme). The non-participation of a di-π-methane route to the ethers was further indicated both by the failure to detect such an intermediate in the crude photolysate and by failure of the cyclopropane (16) to undergo ring-opening under the conditions used for the photolysis of the olefins (3) and (14).

Comparison of the spectrum of the ether (7a) with that of the deuteriated analogue (7b) (Figure b,d) again shows, by the fact that the multiplet at ca. δ 2.3 still integrates for two protons, that C-2 has not incorporated deuterium. The multiplet at δ ca. 2.7, attributed to the methylene group adjacent to the p-methoxyphenyl group, now integrates for one hydrogen. From this evidence it can be concluded that the ether (7) is formed from the ion (17), produced by a 1,3-hydride or deuteride migration within the ion (15), as outlined in route c. This is preferred to route d where two 1,2-shifts are involved.

There is some supportive evidence in the literature for 1,3-hydride transfer in acyclic systems.[11] It has been shown that a small amount of 1,3-hydride shift occurs in the carbocation (18) in its transformation into 3-methyl-

but-1-ene.[12] Such hydride transfers also occur in the deamination of 1-aminopropane.[13] It is obvious, however, that 1,3-hydride transfers do not occur to any great extent in acyclic systems. But the ferrocenyl group has been shown to be better able than *p*-methoxyphenyl group to stabilise a cation on an adjacent carbon [5] and it may be that this is the driving force which tips the balance in favour of the 1,3-hydride transfer within ion (15).

The photochemical addition reaction of an olefin such as (3) is no longer surprising. Previously it had been thought that addition of protic solvents to olefins required the formation of a highly strained *trans*-intermediate as in the photochemical addition to cyclo-

apparatus with a quartz well and a 450-W medium-pressure mercury-arc lamp. The solutions for irradiation were flushed out with oxygen-free nitrogen prior to and during the photolysis.[19] Throughout ether refers to diethyl ether. I.r. spectra were recorded on a Perkin-Elmer 157 spectrometer and n.m.r. spectra on a Perkin-Elmer R10 or Bruker Spectrospin 90 MHz spectrometer.

1-Ferrocenyl-3-*p*-methoxyphenylprop-2-ene-1-one, m.p. 147 °C (lit.,[20] m.p. 150 °C), was prepared by the literature procedure. This compound was converted in 55% yield by the procedure of Watts [5] into 3-ferrocenyl-1-*p*-methoxyphenylprop-1-ene, m.p. 42—43 °C (lit.,[5] m.p. 40—44 °C).

1-*Ferrocenyl*-3-p-*methoxyphenylpropan*-1-*one* (8).—3-*p*-Methoxyphenylpropionyl chloride (2.17 g) was added to aluminium chloride (3 g) in CH_2Cl_2 (100 ml, anhyd.). The
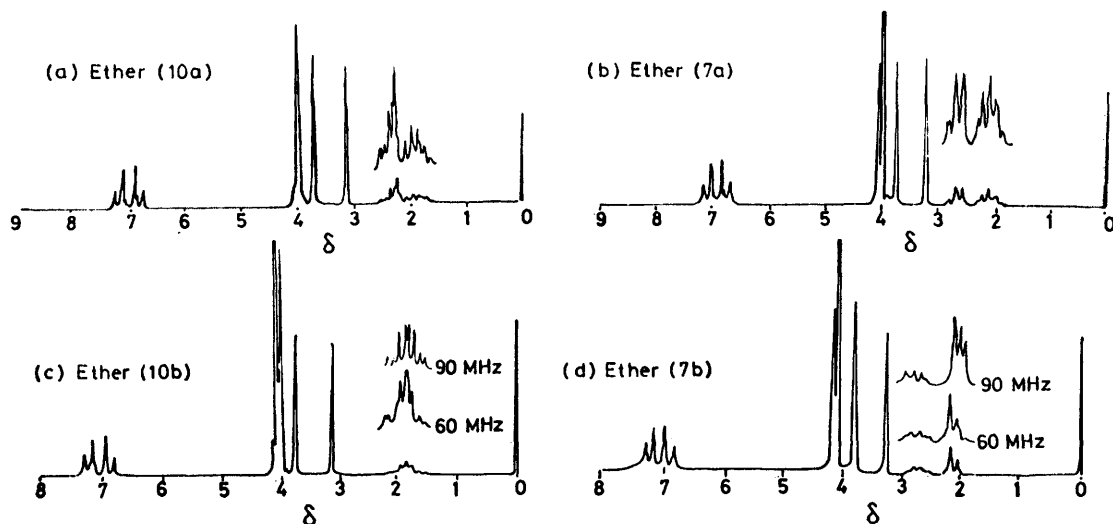

FIGURE [1]H N.m.r. spectra of ethers (10a), (10b), (7a), and (7b)

hexenes and cycloheptenes.[14] However it is now known that photochemical addition does take place to double bonds in acyclic systems provided that electron expulsion occurs [15] or electron-donating groups are present as in our own study of simple ferrocenyl olefins [1] or the work of Nozaki *et al.*[16] and of Hixson [17] who have studied the addition of methanol to several styryl systems (19). The mechanism of the addition in any of these latter systems is not definitely understood although it is likely that photochemical excitation affords a state which is nucleophilic and adds a proton from the solvent to generate a carbocation subsequently trapped by solvent. This is the path which is thought to be involved in the addition of methanol to the propene (3). As yet no evidence has been obtained which implicates the iron atom of the ferrocene in an electron-transfer mode.* Although the involvement of such a process could explain the unexpected reactions encountered in the study of this system a definite statement must await further detailed study.

EXPERIMENTAL

The photolyses were carried out in an immersion-well

* Intramolecular electron transfer from the iron to the carbocation centre has been suggested previously in ground-state reactions.[18]

mixture was stirred for 1 h, filtered through glass wool, and added during 15 min to a solution of ferrocene (2.0 g) in CH_2Cl_2 (100 ml, anhyd.). The mixture was refluxed overnight, cooled, poured onto ice–NH_4Cl and reduced with ascorbic acid. The mixture was extracted with ether (3 × 100 ml). The combined extracts were washed with saturated $NaHCO_3$, water, dried ($MgSO_4$), and evaporated to dryness. Chromatography of the residue on alumina afforded: fraction 1 (eluted with light petroleum–benzene, 1 : 1) ferrocene (0.52 g); fraction 2 (light petroleum–ether, 1 : 1) 1-*ferrocenyl*-3-p-*methoxyphenylpropan*-1-*one* (1.02 g, 35%) as deep red crystals from pentane, m.p. 39—40 °C; $v_{max.}$ (Nujol) 1 710 (C=O) cm^{-1}; δ(CDCl$_3$) 2.95br (s, 4 H), 3.77 (s, 3 H), 4.03 (s), 4.10 (s, 5 H, Fc), 4.42 (t, 2 H, Fc), 4.73 (t, 2 H, Fc), and 6.77—7.26 (m, 4 H, aryl) (Found: C, 69.9; H, 5.9. $C_{20}H_{20}FeO_2$ requires C, 68.57; H, 6.28%).

1-*Ferrocenyl*-3-p-*methoxyphenylpropan*-1-*ol* (9).—To a solution of 1-ferrocenyl-3-*p*-methoxyphenylpropan-1-one (0.5 g) in ether (100 ml, anhyd.) was added during 15 min, lithium aluminium hydride (0.4 g) in ether (20 ml, anhyd.). The mixture was stirred overnight and then worked up and the residue chromatographed on alumina to yield: fraction (1) (ether) recovered 1-ferrocenyl-3-*p*-methoxyphenylpropan-1-one (0.15 g, 30%); fraction (2) (ether): 1-*ferrocenyl*-3-p-*methoxyphenylpropan*-1-*ol* (0.25 g, 51%) as a yellow oil; $v_{max.}$ (liq. film) 3 400 (OH) cm^{-1}; δ(CDCl$_3$)

1.71—2.24 (m, 2 H), 2.49—2.85 (m, 2 H), 2.07 (s, 1 H collapsing on addition of D_2O), 3.69 (s, 3 H), 4.09 (s), 4.14 (s, 10 H), and 6.74—7.22 (4 H, aryl). Analysis of this compound was not possible owing to its rapid decomposition.

3-*Ferrocenyl-3-methoxy*-1-p-*methoxyphenylpropane* (7a).— 1-Ferrocenyl-3-p-methoxyphenylpropan-1-ol (0.28 g) in methanol (75 ml) and formic acid (0.5 ml) was stirred for 2 h at room temperature. The reaction mixture was quenched with saturated $NaHCO_3$ and worked up. Chromatography of the residue on alumina afforded: fraction (1) (light petroleum–ether, 1 : 1) 3-*ferrocenyl-3-methoxy*-1-p-*methoxyphenylpropane* (0.19 g, 65%) as a yellow oil; $v_{max.}$ (liq. film) 3 040—2 890 (alkyl), 1 600, 1 560, 1 510, and 745 (aryl); 1 100, 1 000, and 830—805 (FcH); 1 090, 1 055, and 1 040 (OCH$_3$) cm^{-1}; δ(CDCl$_3$) 1.80—2.22 (m, 2 H), 2.52—2.68 (m, 2 H), 3.20 (s, 3 H), 3.73 (s), 3.95br (s), 4.03 (s, 10 H, Fc + C-3-H), and 6.58—7.06 (m, 4 H, aryl) (Found: C, 69.35; H, 6.55. C$_{21}$H$_{24}$FeO$_2$ requires C, 69.2; H, 6.60%).

3-*Ferrocenyl*-1-p-*methoxyphenylpropane* (6) *and* 3-*Ferro-cenyl*-1-*methoxy*-1-p-*methoxyphenylpropane* (10a).—3-Ferro-cenyl-1-p-methoxyphenylprop-1-ene-3-ol (3.0 g), prepared by the reduction of 1-ferrocenyl-3-p-methoxyphenylprop-2-en-1-one in dioxan with sodium borohydride and used without purification, was stirred with silica (2 g) in methanol (175 ml) for 24 h. The solid was filtered off and water (30 ml) added to the filtrate. The mixture was extracted into ether and the extracts washed with water, dried (MgSO$_4$), filtered, and the excess of solvent removed. The residue, a yellow oil, was chromatographed rapidly on alumina with solvent ether to yield a yellow oil (2.48 g). N.m.r. analysis indicated that this was a mixture of 3-ferro-cenyl-3-methoxy-3-p-methoxyphenylprop-1-ene (60%) and 3-ferrocenyl-1-methoxy-1-p-methoxyphenylprop-2-ene (40%). Attempts to separate the mixture by careful chromatography proved impossible because of extensive decomposition of the compounds on long exposure on alumina. The mixture of alkenyl ethers (2.48 g) was reduced in cyclohexane (100 ml) using Pd–C (1 g, 30%) as catalyst and H$_2$ (180 ml at 1 atm). After 30 min the reduction was complete, the Pd–C catalyst was filtered off, excess of solvent was evaporated, and the yellow oily residue chromatographed on alumina to yield: fraction (1) (light petroleum–ether, 9 : 1) 3-ferrocenyl-1-p-methoxyphenylpro-pane (0.47 g, 20%) as orange crystals from pentane, m.p. 42—43 °C; $v_{max.}$ (Nujol) 1 600, 1 570, 1 510, and 755 (aryl); 1 100, 995, and 830—805 (FcH); 1 040 and 1 020 (OCH$_3$); 3 000—2 800 cm^{-1} (alkyl); δ(CDCl$_3$) 1.57—1.95 (m), 2.06—2.63 (m, 6 H, alkyl), 3.65 (s, 3 H), 3.90 (s), and 3.84 (s, 9 H), 6.62—7.07 (m, 4 H, aryl) (Found: C, 72.85; H, 6.75. C$_{20}$H$_{22}$FeO requires C, 72.85; H, 6.58%). Fraction (2): (light petroleum–ether, 7 : 3) 3-*ferrocenyl-1-methoxy*-1-p-*methoxyphenylpropane* (1.46 g, 59%) as a yellow viscous oil, b.p. 125 °C/0.2 mmHg; $v_{max.}$ (liq. film) 3 040—2 890 (alkyl), 1 600, 1 560, 1 510, and 745 (aryl); 1 100, 1 000, and 830—810 (Fc); 1 090, 1 055, and 1 040 cm^{-1} (OCH$_3$); δ(CDCl$_3$) 1.66—2.03 (m, 2 H), 2.14—2.47 (m, 2 H), 3.08 (s, 3 H), 3.68 (s, 3 H), 3.85br (s, 10 H, Fc + C-1-H), and 6.58—7.06 (m, 4 H, aryl) (Found: C, 69.6; H, 6.45. C$_{21}$H$_{24}$FeO$_2$ requires C, 69.20; H, 6.6%). Fraction (3) (light petroleum–ether, 1 : 1) 3-ferrocenyl-3-methoxy-1-p-methoxypropane (0.37 g, 15%) as an orange-yellow viscous oil.

Photolysis of 3-*Ferrocenyl*-1-p-*methoxyphenylprop*-1-*ene in Methanol*.—The olefin (1.53 g) in methanol (300 ml), degassed by passage of oxygen-free nitrogen for 1 h, was

photolysed through quartz for 16 h. The crude reaction solution was poured into water (500 ml) and worked up. Chromatography on alumina (deactivated by exposure to the atmosphere for 2 days) yielded: fraction (1) (light petroleum–ether, 8 : 2) 3-ferrocenyl-1-p-methoxyphenylpro-pane (0.06 g, 1%); fraction (2) (light petroleum–ether, 1 : 1) 3-ferrocenyl-1-p-methoxyphenylprop-1-ene (0.8 g, 43%); fraction (3) (light petroleum–ether, 1 : 1) 3-ferrocenyl-1-methoxy-1-p-methoxyphenylpropane (0.72 g, 38.5%); fraction (4) (light petroleum–ether, 1 : 1) 3-ferrocenyl-3-methoxy-1-p-methoxyphenylpropane (0.24 g, 14%).

Photolysis of 3-*Ferrocenyl*-1-*methoxy*-1-p-*methoxyphenyl-propane in Methanol*.—The ether (0.30 g), Na$_2$CO$_3$ (2.0 g, anhyd.) in a stirred solution of methanol (200 ml) was de-gassed with N$_2$[O$_2$ free] for 1 h and then photolysed through quartz for 16 h. The reaction solution was poured into water (500 ml) and worked up. Chromatography on de-activated alumina afforded: fraction (1) (light petroleum–ether, 9 : 1) 3-ferrocenyl-1-p-methoxyphenylpropane (0.038 g, 13%); fraction (2) (light petroleum–ether, 9 : 1) 3-ferro-cenyl-1-methoxy-1-p-methoxyphenylpropane (0.034 g, 11%).

Photolysis of 3-*Ferrocenyl-3-methoxy*-1-p-*methoxyphenyl-propane in Methanol*.—The ether (0.35 g), Na$_2$CO$_3$ (2.0 g, anhyd.) in a stirred solution of methanol (200 ml) was degassed with N$_2$(O$_2$ free) for 1 h, and then photolysed through quartz for 15 h. The reaction solution was poured into water (500 ml) and worked up as above. Chromato-graphy of the oily residue afforded: fraction (1) (light petroleum–ether, 9 : 1) 3-ferrocenyl-1-p-methoxyphenylpro-pane (0.035 g, 10%); fraction (2) (light petroleum–ether, 9 : 1) 3-ferrocenyl-3-methoxy-1-p-methoxyphenylpropane (0.080 g, 25%).

3,3-*Dideuterio-3-ferrocenyl*-1-p-*methoxyphenylprop*-1-*ene* (14).—1-Ferrocenyl-1-p-methoxyphenylprop-2-en-1-one (4.5 g) was added portionwise to a stirred suspension of lithium aluminium deuteride (0.6 g) and aluminium chloride (5.0 g) in ether (100 ml, anhyd) and the mixture was stirred until all the ketone had reacted as indicated by t.l.c. analysis. The reaction was quenched in ice–water (400 ml) and the ether layer separated. The total extract was dried (MgSO$_4$) and evaporated, and the residue was dissolved in light petroleum and chromatographed on alumina to yield: fraction (1) (light petroleum–ether, 8 : 2) 3,3-*dideuterio*-3-*ferrocenyl*-1·p-*methoxyphenylprop*-1-*ene* (3.80 g, 86%) as orange-yellow crystals from pentane, m.p. 57—58.5 °C; $v_{max.}$ (Nujol) 1 100, 990, and 835—810 (FcH); 1 100 and 1 015 (OCH$_3$); 1 295 and 965 cm^{-1} (C=C); δ(CDCl$_3$) 3.54 (s, 3 H, OMe), 4.00 (s), and 4.05 (s, 9 H, Fc), 6.22 (dd, $J = 15$ Hz, 2 H), and 6.70—7.31 (m, 4 H, aryl); mass spectrum accurate mass determination (Found: M^+, 334.098 0. C$_{20}$H$_{18}$D$_2$FeO requires M, 334.098 0).

Photolysis of 3,3-*Dideuterio-3-ferrocenyl*-1-p-*methoxy-phenylprop*-1-*ene in Methanol*.—Freshly prepared dideuterio-olefin (2.0 g) in methanol (200 ml), degassed by passage of N$_2$(O$_2$ free) for 2 h was photolysed through quartz for 16 h. The reaction solution was poured into water (500 ml) and worked up. Chromatography of the oily residue afforded: fraction (1) (light petroleum ether, 19 : 1) 3,3-dideuterio-3-ferrocenyl-1-p-methoxyphenylpropane and other D iso-mers (0.049 g, 2.5%), a yellow mobile oil; fraction (2) (light petroleum–ether, 9 : 1) 3,3-dideuterio-3-ferrocenyl-1-p-methoxyphenylprop-1-ene (0.664 g, 33%) as orange needles from pentane, m.p. 57—58.5 °C; fraction (3) (light petroleum–ether, 9 : 1) 3,3-*dideuterio-3-ferrocenyl*-1-*methoxy*-

1-p-*methoxyphenylpropane* (10b) (0.525 g, 24%) as a viscous orange oil, b.p. 160 °C/0.33 mmHg; $\nu_{max.}$ (liq. film) 1 100, 995, and 840—790 (FcH); 1 610, 1 580, 780, and 725 (aryl); 1 080, 1 060, 1 030, and 1 020 cm⁻¹ (OCH₃); δ(CDCl₃) 1.70—2.00 (m, 2 H), 3.10 (s, 3 H), 3.70 (s, 3 H), and 3.95br (s) and 4.00br (s, 10 H, 9Fc + C-1, H); mass spectrum accurate mass determination (Found: M^+, 366.120 02. $C_{21}H_{22}D_2FeO_2$ requires M, 366.125 107); fraction (4) (light petroleum–ether, 9 : 1) 1,3-*dideuterio-3-ferrocenyl-3-methoxy-1-p-methoxyphenylpropane* (7b) (0.136 g, 6%) as an orange oil, b.p. 180 °C/0.4 mmHg (some decomposition); $\nu_{max.}$ (liq. film) 1 100, 995, and 820—800 (Fc); 1 600, 1 570, 1 510, and 750 (aryl); 3 100—2 820 (alkyl); 1 080, 1 060, and 1 030 cm⁻¹ (OCH₃); δ(CDCl₃) 2.0—2.3 (m, 2 H), 2.9—2.5 (m, 1 H), 3.25 (s, 3 H), 3.80 (s, 3 H), 4.05br (s), and 4.10br (s, 9 H); mass spectrum accurate mass determination (Found: M^+, 366.124 546. $C_{21}H_{22}D_2FeO_2$ requires M, 366.125 107).

Photolysis of 1-Ferrocenyl-1-methyl-3,3-diphenylcyclopropane in Methanol (16).—The cyclopropane [21] (1.00 g) in methanol (200 ml) was degassed for 3 h using $N_2(O_2$ free) and then photolysed through quartz for 17 h. The reaction solution was poured into water and worked up. Chromatography of the oily residue yielded: fraction (1) (light petroleum–ether, 9 : 1) 1-ferrocenyl-1-methyl-3,3-diphenylcyclopropane (0.821 g, 82%). Quantities of decomposed material remained at the top of the column.

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