Photochemistry of (Ferrocenylmethyl)triphenylphosphonium Salts

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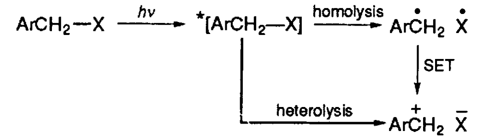
The photochemistry of (ferrocenylmethyl)triphenylphosphonium salts in acetonitrile and in acetonitrile–alcohols/amines is investigated. In acetonitrile, the only ferrocenyl product arises from reactions of ferrocenylmethyl radicals, whilst in mixtures of acetonitrile–alcohols/amines, high yields of the photosolvolysis products are obtained. The effect of the phosphonium salt counterion is investigated and a mechanism is proposed to account for the product distribution. The possible role of the metal in the reactions is discussed.

Interest has arisen recently in photochemical reactions which lead to the generation of free radicals and carbocations in the same process.[1] Much of the research activity has been directed towards understanding the photochemistry of benzylic compounds. In the photodecomposition of those systems, it is generally believed that the carbocation can arise from at least two different pathways, either intermolecular electron transfer from the benzyl radical generated in a primary bond cleavage step to some electron-accepting species, or by direct bond heterolysis (Scheme 1). Some benzylic derivatives, most notably benzyl phosphate esters[1r] favour the direct bond heterolysis route to the carbocation whereas the results of most studies are not conclusive on this issue.



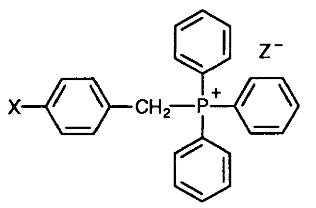
$X = I, Br, \overset{+}{P}Ph_3, \overset{+}{N}Me_3, OC(O)CH_2Ph, SR', SeR', OP(O)(OEt)_2, \overset{+}{S}R_2$

Scheme 1

We have recently studied the photodecomposition of a series of benzyltriphenylphosphonium halides and tetrafluoroborates **1** in acetonitrile and methanol.[2] In all cases, the non-phosphorus products include materials derived from benzyl radicals and benzyl carbocations. The relative percentage of products derived from radical *versus* ionic intermediates varied according to the nature of the substituent X, the oxidizability of the counterion-(Z^-), or the nature of the remaining aryl groups attached to phosphorus. For the compounds where (Z^-) is the non-oxidizable tetrafluoroborate counterion, we observed that the percentage of ionic product to radical product showed a non-linear relationship with the Hammett constant of the substituent X. The amount of ionic product was much lower than expected in the photodecomposition of *p*-methoxybenzyltriphenylphosphonium tetrafluoroborate in either acetonitrile or methanol; this was ascribed to either a Marcus effect[3] or an internal return effect (or a combination of both). To investigate further the role of the carbocation in this type of reaction, we decided to include in our studies substrates in which the substituted benzyl group in **1** has been replaced by a ferrocenylmethyl group.

The ferrocenylmethyl carbocation and other ferrocenylalkyl carbocations are particularly thermally stable.[4] For example, the $pK_R{}^+$ value of hydroxymethylferrocene is -1.49,[4g] compared to values of -13.3 for diphenylmethanol and -6.63 for triphenylmethanol.

Despite the intensive studies of ferrocenylalkyl carbocations, less is known about ferrocenylalkyl radicals. Recently, Jackson *et al.*,[5] reported on the structure of the ferrocenylmethyl radical using EPR spectroscopy after generating the radicals by the irradiation of methylferrocene in an adamantane matrix. Prior to that study, Baker and Horspool[6] generated ferrocenylmethyl radicals and other ferrocenylalkyl radicals by the photolysis of ferrocenylalkyl ethers in methanol. For example, the photolysis of ethyl ferrocenylmethyl ether in methanol produced methylferrocene **3**, 1,2-diferrocenylethane **4** and methyl ferrocenylmethyl ether **5** (Scheme 2). The first two products are typical radical products whilst the ether **5** presumably arises from a photosolvolysis process.



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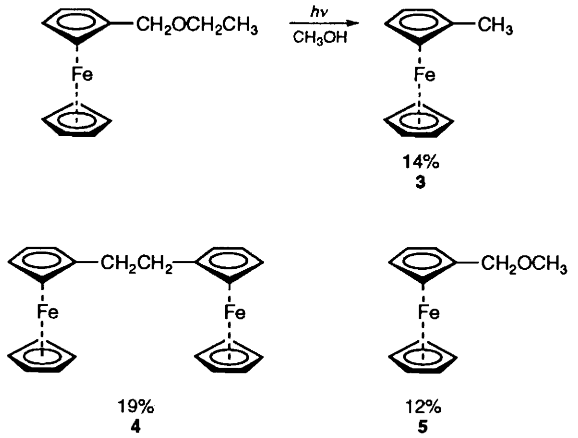
$X = NO_2, CN, Cl, F, H, Me, Bu^t, MeO$
$Z = Cl, Br, I, BF_4$



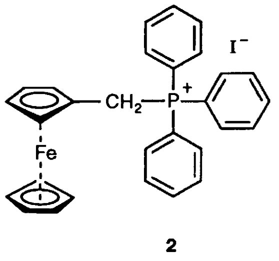
Scheme 2

For these reasons, we decided to investigate the photochemistry of (ferrocenylmethyl)triphenylphosphonium salts and in this paper, our results on the photodecomposition of (ferrocenylmethyl)triphenylphosphonium iodide **2** at 254 nm in various solvent systems are reported. The results show that

Table 1 Yields of products for the photodecomposition of (ferrocenylmethyl)triphenylphosphonium iodide **2** in various solvent systems at 254 nm (35 °C)

Solvent system[a]	Product X	$FcCH_2X$ Isolated yield (%)[b]
CH_3CN	H	73
CH_3CN-MeOH	OMe	91
CH_3CN-EtOH	OEt	60
CH_3CN-H_2O	OH	62
CH_3CN-$(Pr^i)_2NH$	$N(Pr^i)_2$	54

[a] The ratio of mixed solvents is 4:1 (v/v) (CH_3CN–ROH or R_2NH). [b] Thermal experiments were carried out simultaneously. Compound **2** was thermally stable in acetonitrile but we found that 1–2% of the isolated yield of $FcCH_2X$ compound was formed by a thermal process.



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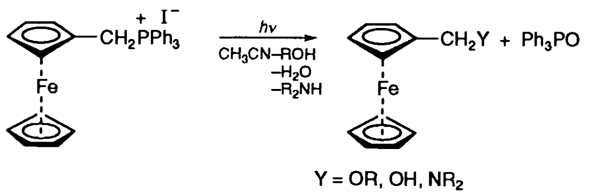
compound **2** can, as with ferrocenylmethyl ethers, serve as a source of ferrocenylmethyl radicals and ferrocenylmethyl carbocations according to the composition of the solvent in which the reaction is carried out.

Results and Discussion

Compound **2** was synthesized according to the procedure of Pauson and Watts.[7] The results for the photodecomposition of **2** are shown in Table 1. In pure acetonitrile, only methylferrocene was isolated in good yield. We assume that this product arises by the reaction of ferrocenylmethyl radicals with the solvent. Evidence for the involvement of ferrocenylmethyl radicals in this reaction was obtained by repeating the reaction in acetonitrile saturated with oxygen. In this instance, a good yield of ferrocenecarboxaldehyde was obtained together with a trace of methylferrocene. Clearly, trapping ferrocenylmethyl radicals with oxygen could be expected to give ferrocenecarboxaldehyde, in analogy to the known formation of aldehydes in the thermal decomposition of alkanes in the presence of oxygen.[8] The photodecomposition of **2** in solvent mixtures consisting of acetonitrile–alcohols, acetonitrile–water and acetonitrile–amines, gave only ferrocene-containing products arising from reaction of ferrocenylmethyl carbocations with the more nucleophilic component of the solvent mixture (Scheme 3).



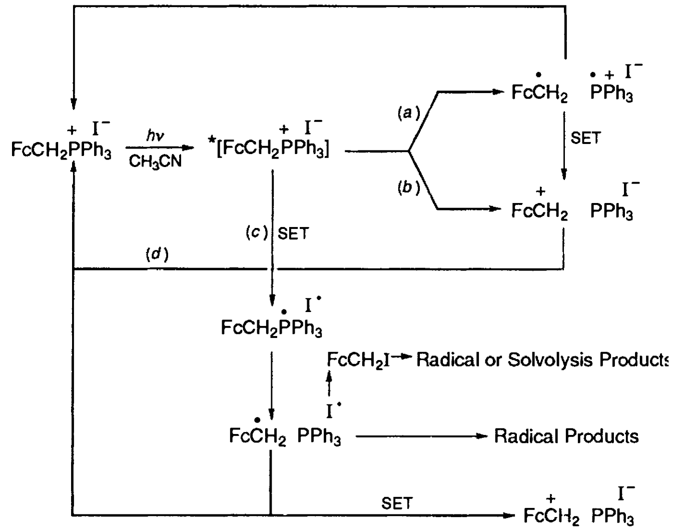
Scheme 3

These reactions in mixed solvent systems represent a new route to compounds of the type $FcCH_2X$ (X = OR, NR_2). The results can be compared with those obtained in our earlier work for the photodecomposition of benzyltriphenylphosphonium iodide in acetonitrile and methanol.[2] In acetonitrile, *N*-benzylacetamide (9%) was formed (this product arises from the reaction of benzyl carbocations with acetonitrile, followed by hydrolysis), as well as products derived from benzyl radicals (toluene and bibenzyl). In methanol, photodecomposition of benzyltriphenylphosphonium iodide also gave non-phosphorus products derived from benzyl radicals and benzyl carbocations.

Compound **2** is thermally stable in acetonitrile under the conditions of the photolysis but in solvent mixtures such as acetonitrile–alcohols, a small amount (< 5%) of **2** decomposes to give the solvolysis products. The compounds forming during the photochemical reactions with **2** are all reasonably stable under the reaction conditions with the (alkoxymethyl)ferrocenes showing some degree of C_p–Fe bond cleavage but not showing the type of photochemistry observed by Baker and Horspool[6] (this difference must reflect the use of different UV lamps). Addition of tributyltin hydride, a good hydrogen donor molecule[9] to reaction mixtures of **2** in acetonitrile–alcohol produced upon irradiation some methylferrocene in addition to the ether product. Increasing the concentration of the tin hydride led to increased yields of methylferrocene with respect to the photosolvolysis products.

The irradiation of **2** in pure methanol gave a very slow reaction and the conversion to the solvolysis product was very low even after long irradiation times. Furthermore, the irradiation of the tetrafluoroborate salt of **2** in either pure acetonitrile or pure methanol at 254 nm showed negligible reaction after long periods of irradiation. These observations give evidence that the iodide ion plays an important role in the photodecomposition of **2**.

The mechanism shown in Scheme 4 highlights some of the possible routes to ferrocenylmethyl radicals and carbocations from **2** and is similar to the model which we used to explain the photodecomposition of benzyltriarylphosphonium salts.[2] On photolysis, compound **2** undergoes excitation followed by the homolysis or heterolysis of the CH_2–P^+ bond to give either a ferrocenylmethyl radical–triphenylphosphine radical cation intimate pair [route (*a*)] or a ferrocenylmethyl carbocation–triphenylphosphine pair [route (*b*)]. Single electron transfer (SET) from the ferrocenylmethyl radical to the triphenylphosphine radical cation offers an alternative indirect route to the ferrocenylmethyl carbocation. An alternative route to ferrocenylmethyl radicals from **2**, as suggested before for other phosphonium ions,[10] is *via* single electron transfer from the highly oxidizable iodide counter ion onto the phosphorus centre producing a phosphoranyl radical [route (*c*)]. Radicals of this type decompose rapidly by α-scission[11] giving in this case ferrocenylmethyl radicals and triphenylphosphine. This charge transfer must be dependent on the nature of the counterion and

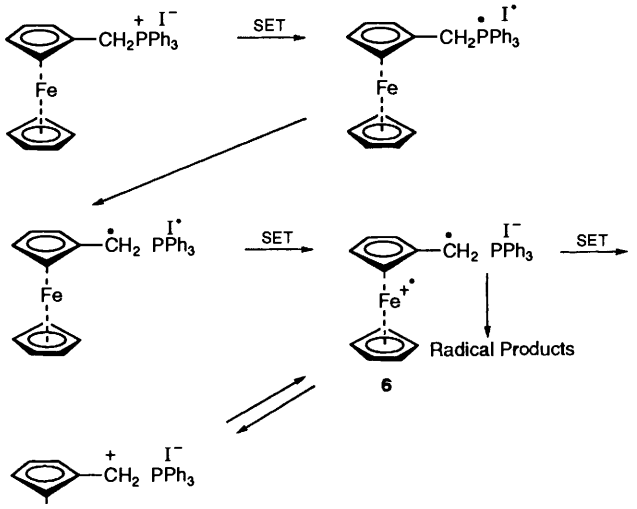


Scheme 4

the solvent; in methanol, ions are solvated more efficiently than in acetonitrile and so the charge transfer becomes more difficult as the concentration of methanol increases. Furthermore, the charge transfer mechanism cannot operate if the counterion is non-oxidizable (tetrafluoroborate).

Photolysis of **2** in acetonitrile gives methylferrocene arising from the reaction of ferrocenylmethyl radicals with a hydrogen source (solvent or tin hydride). This result compared to that obtained from benzyltriphenylphosphonium iodide[2] (9% of *N*-benzylacetamide) can be explained in terms of the difference in reactivity of benzyl and ferrocenylmethyl carbocations with acetonitrile. It has been shown independently by Ceccon *et al.*,[12] that ferrocenylmethyl carbocations do not react with acetonitrile at low temperatures and so in acetonitrile, even if ferrocenylmethyl carbocations are generated by either heterolysis or SET, internal return (reaction of the ferrocenylmethyl-carbocation with triphenylphosphine to give starting material) will be favoured [route (*d*)]. The carbocation is thus removed from the system and so only the radical-derived product is isolated. On introducing a more nucleophilic component into the acetonitrile solution such as an alcohol or amine, photosolvolysis now competes with the internal return reaction and the photosolvolysis products are isolated in good yields. In these mixed solvents, radical products were not detected or isolated although the results obtained by addition of tin hydride indicate that ferrocenylmethyl radicals are formed.

Our mechanistic interpretation assumes that iron takes no direct part in the reaction. It is however possible to propose a mechanism involving oxidation of the metal by an iodine atom after the initial steps involving SET and α-cleavage of the phosphoranyl radicals (Scheme 5). It gives a diradical cation **6** which could undergo intramolecular SET to produce a ferrocenylmethyl carbocation. The driving force for this intramolecular SET process should be large because of the stability of the ferrocenylmethyl carbocation. The concept of an equilibrium between the diradical cation **6** and carbocation is not new in organometallic chemistry and has been used previously by several groups.[6,13]



Scheme 5

In conclusion, we have demonstrated that the stability of the arylmethyl carbocation (*e.g.* ferrocenylmethyl *versus* benzyl) has a profound effect on the product distribution and selectivity in the photolysis of the corresponding phosphonium salts. Also, we have provided a new synthetic route to compounds of the type $FcCH_2X$ ($X = OR, NR_2$).

Experimental

All reactions were carried out under nitrogen or argon. Silica gel was used for column chromatography. Infra-red spectra were recorded using a Bomem FT-IR spectrometer. NMR spectra were recorded on a Bruker AC 300 spectrometer with TMS (^1H) as an internal or 85% H_3PO_4 (^{31}P) as an external standard. Photochemical experiments were carried out in a Rayonet Model RPR-208 photochemical reactor fitted with a merry-go-round attachment and 253.7 nm lamps. GC analysis was performed using a Varian 3700 gas chromatograph linked to a Varian 4270 recorder/integrator. A 25 m long glass capillary column of 0.3 mm inner diameter with a 0.3 μm thick stationary phase film of polymethylsiloxane (SE30) was used throughout. The analysis of the reaction products was carried out as follows. Tentative identification was obtained from the ^1H NMR spectra of the mixtures. Suspected products were independently prepared and their solutions were injected into the gas chromatograph. The products were identified by co-injection of a sample and the standard solution. Products were then isolated using column chromatography. Acetonitrile was dried over calcium hydride.

Authentic samples of ferrocene derivatives produced during the photochemical reactions were synthesized by independent methods. Ferrocenecarboxaldehyde was synthesized by the photochemical reaction of ferrocene in a chloroform–ethanol solvent mixture,[14] m.p. 126 °C, lit.,[15] 124–125 °C, $\delta_H(CDCl_3)$ 4.30 (s, 5 H, C_5H_5), 4.60 (t, 2 H, CH_2), 4.80 (t, 2 H, CH_2) and 9.90 (s, 1 H, CHO). Methylferrocene was prepared by the reduction of (ferrocenylmethyl)triphenylphosphonium iodide with lithium aluminium hydride.[7] Hydroxymethylferrocene was prepared by the reaction of *N*,*N*-dimethylaminomethylferrocene methiodide and sodium hydroxide.[16] Methyl ferrocenylmethyl ether and ethyl ferrocenylmethyl ether were prepared by the reaction of *N*,*N*-dimethylaminomethylferrocene methiodide with methanol and ethanol.

(Ferrocenylmethyl)triphenylphosphonium Iodide.—The title compound was prepared according to the procedure of Pauson and Watts;[7] m.p. 254–256 °C (decomp.), (lit.,[7] 254–256 °C); $\nu_{max}(KBr)/cm^{-1}$ 1482, 1419, 1105, 922, 828 and 741; $\delta_H(CDCl_3)$ 4.01 (d, 4 H, C_5H_4), 4.30 (s, 5 H, C_5H_5), 4.90 (d, 2 H, *J* 11.7, CH_2) and 7.24–7.76 (m, 15 H, Ph); $\delta_P(CDCl_3)$ 19.69; *m*/*z* 263 (19%), 262 (100), 261 (14), 200 (6), 199 (24), 185 (10) and 184 (14).

(Ferrocenylmethyl)triphenylphosphonium Tetrafluoroborate.—(Ferrocenylmethyl)triphenylphosphonium iodide (0.5 g, 0.85 mmol) was dissolved in the minimal amount of hot water. To this solution was added sodium tetrafluoroborate (1.0 g, 9 mmol) dissolved in water. A yellow solid was filtered, dried, and recrystallized from acetonitrile–diethyl ether and identified as (ferrocenylmethyl)triphenylphosphonium tetrafluoroborate (0.2 g, 43%), m.p. 225–227 °C (decomp.); $\nu_{max}(KBr)/cm^{-1}$ 1437, 1066, 748, 692 and 489 (Found: C, 63.0, H, 4.7. $C_{29}H_{26}BF_4FeP$ requires C, 63.54; H, 4.78%); $\delta_H(CDCl_3)$ 3.87 (d, 2 H, C_5H_4), 4.03 (d, 2 H, C_5H_4), 4.25 (s, 5 H, C_5H_5), 4.52 (d, 2 H, *J* 11.7, CH_2) and 7.50–7.77 (m, 15 H, Ph); $\delta_P(CDCl_3)$ 19.42; *m*/*z* 263 (21%), 262 (100), 186 (8), 185 (9) and 184 (12).

Photolysis of (Ferrocenylmethyl)triphenylphosphonium Iodide. General Procedure.—(Ferrocenylmethyl)triphenylphosphonium iodide (82 mg) was dissolved in anhydrous solvent (10 cm^3) and the solution was degassed using argon for 30 min. The solutions were irradiated at 254 nm for varying periods depending on the extent of decomposition. The solutions were analysed by GLC and NMR spectroscopy to identify the products. The reaction mixtures were then separated using column chromatography and the pure products were isolated. Yields of products are given in Table 1.

Photolysis of (ferrocenylmethyl)triphenylphosphonium iodide. (*a*) *In acetonitrile.* Products isolated were methylferrocene, m.p. 35–36 °C (lit.,[7] 34–36 °C); $\delta_H(CDCl_3)$ 1.97 (s, 3 H, CH_3), 4.0 (t, 2 H, C_5H_4), 4.04 (t, 2 H, C_5H_4) and 4.07 (s, 5 H, C_5H_5); *m/z* 200 (M^+); and triphenylphosphine oxide, $\delta_P(CDCl_3)$ 29.84.

In acetonitrile saturated with O_2. Product isolated was ferrocenecarboxaldehyde (69%), identical to the standard. GLC showed also traces of **3** and hydroxymethylferrocene.

(*b*) *In acetonitrile–methanol.* Products isolated were methyl ferrocenylmethyl ether, identical to the independently prepared sample; $\delta_H(CDCl_3)$ 3.29 (s, 3 H, CH_3), 4.09 (s, 5 H, C_5H_5), 4.12 (t, 2 H, C_5H_4), 4.21 (t, 2 H, C_5H_4) and 4.20 (s, 2 H, CH_2); and triphenylphosphine oxide.

(*c*) *In acetonitrile–ethanol.* Products isolated were ethyl ferrocenylmethyl ether, identical to the independently prepared sample; $\delta_H(CDCl_3)$ 1.16 (t, 3 H, CH_3), 3.46 (q, 2 H, CH_2), 4.09 (s, 5 H, C_5H_5), 4.12 (t, 2 H, C_5H_4), 4.21 (t, 2 H, C_5H_4) and 4.25 (s, 2 H, CH_2); and triphenylphosphine oxide.

(*d*) *In acetonitrile–water.* Products isolated were hydroxymethylferrocene, m.p. 82 °C, (lit.,[16] 81–82 °C); $\delta_H(CDCl_3)$ 4.15 (t, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.22 (t, 2 H, C_5H_4) and 4.31 (s, 2 H, CH_2); and triphenylphosphine oxide.

(*e*) *In acetonitrile–diisopropylamine.* Products isolated were (ferrocenylmethyl)diisopropylamine; $\delta_H(CDCl_3)$ 0.99 (d, 12 H, 4 × CH_3), 1.18 (m, 2 H, 2 × CH), 3.44 (s, 2 H, CH_2), 4.02 (t, 2 H, C_5H_4), 4.06 (s, 5 H, C_5H_5) and 4.16 (t, 2 H, C_5H_4); *m/z* 299 (M^+, 2.2%), 244 (8), 199 (36) and 185 (2); and triphenylphosphine oxide.

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