Stable Carbocations. Part 19.[1] A Kinetic Study of the Fragmentation of Ferrocenyldiarylmethylium Ions in Aqueous Acidic Acetonitrile

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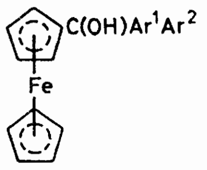
Rate constants have been measured for the spontaneous fragmentation of ferrocenyldiarylmethylium ions $Fc\overset{+}{C}Ar^1Ar^2$ in aqueous acidic acetonitrile giving 6,6-diarylpentafulvenes. The reaction rate is sensitive to the presence of *para*-substituents (OMe or CF_3) in the aryl rings and to change in the ionic strength of the medium. Factors influencing fragmentation of ferrocenylcarbocations are discussed.

ALTHOUGH secondary ferrocenylcarbocations of the type $Fc\overset{+}{C}HAr$ (Ar = aryl or Fc) are stable in aqueous acidic solutions in which they exist in equilibrium with the corresponding alcohols FcCH(OH)Ar,[2,3] tertiary diaryl analogues (2) decompose spontaneously in such media with liberation of the 6,6-diarylpentafulvene ligand (3). Reactions of this type were first reported [4a] in 1964 and have been noted subsequently as complicating side-reactions during pK_{R^+} measurements.[2,3] Scission of the iron–pentafulvene ligand bond also occurs when solutions of ferrocenylcarbocation salts are irradiated.[4b] Since the mechanism of the process has not been studied, we have carried out a product and kinetic study of the reaction in aqueous acidic acetonitrile.[5]



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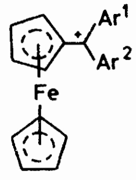

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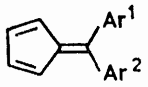


(3)

a; $Ar^1 = Ar^2 = Ph$
b; $Ar^1 = Ph, Ar^2 = p\text{-}MeOC_6H_4$
c; $Ar^1 = Ar^2 = p\text{-}MeOC_6H_4$
d; $Ar^1 = Ph, Ar^2 = p\text{-}F_3CC_6H_4$

Product Studies.—The ferrocenyldiarylmethylium ions (2a—d) were generated quantitatively when the corresponding alcohols (1a—d) were dissolved in concentrated H_2SO_4 or neat CF_3CO_2H and were moderately stable in these solvents; the ^1H n.m.r. spectra (see Experimental section) of solutions in CF_3CO_2H, for example, showed only slow deterioration with time. Furthermore, BF_4^- and ClO_4^- salts, prepared by Allenmark's method,[6] were fairly stable as solids and in solution in anhydrous MeCN or $(CH_2Cl)_2$. Addition of NaOH in water or NaOMe in methanol to fresh solutions in MeCN gave quantitative yields of the addition products (1) and $FcC(OMe)Ar^1Ar^2$ respectively.

However, in solution in aqueous MeCN containing HCl or H_2SO_4, equilibrium mixtures of the alcohols (1a—d) and related carbocations (2a—d) decomposed within a few hours giving solutions from which the corresponding pentafulvenes (3a—d) were isolated. These were identified from their spectroscopic properties, which have been reported [7] earlier for compounds (3a—c), and for (3a) by comparison with an authentic sample prepared by base-catalysed condensation of benzophenone and cyclopentadiene. Independent experiments established that the spontaneous fragmentation reaction is neither light- nor oxygen-catalysed.

In these reactions, the $CpFe^+$ fragment expelled from the cations (2) broke down further to inorganic iron salt(s) and, presumably, cyclopentadiene which was not identified. No evidence for the formation of Cp_2Fe, Cp_2Fe^+, or $[CpFe(NCMe)_3]^+$ was found. Attempts to trap this fragment with good 6π-electron donor ligands were unsuccessful. Thus, when (2a) was allowed to decompose to (3a) in the presence of a large excess of mesitylene, no trace of the known [8] complex $[CpFe(\eta^6\text{-mesitylene})]^+$ was found in the product. Similarly, decomposition of (2a) in the presence of 6,6-dimethylpentafulvene did not lead to the formation of $[CpFe(\eta^6\text{-dimethylpentafulvene})]^+$, *i.e.*, $Fc\overset{+}{C}Me_2$, since derived neutral products [9] were absent.

Kinetic Studies.—The previous experiments establish that the cations (2) fragment, releasing the pentafulvene ligand (3), in aqueous acidic media in which repeated reversible formation from the alcohol precursors (1) occurs. The effect of change in acid strength was investigated by kinetic experiments in which the rates of formation of the pentafulvenes in H_2O–MeCN (1 : 1 w/w) containing HCl at various molarities were measured spectroscopically (see Experimental section). The reactions were first order through at least four half-lives and duplicate runs gave acceptable agreement; representative pseudo-first-order rate constants (k_ψ) at selected acid concentrations are in Table 1. Similar k_ψ values were obtained from related experiments [5] in which H_2SO_4 was used as proton source. At the acid concentrations used, therefore, H_2SO_4 must behave as a monoprotonic acid in the aqueous organic solvent.[10]

In kinetic terms, reaction (1) takes place. The rate

$$H^+ + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + R^+ \xrightarrow{k_2} \text{pentafulvene} \quad (1)$$

constants k_1 and k_{-1} (with $k_1/k_{-1} = K_{R^+}$) for interconversion of (1a—c) and (2a—c) in the same solvent have been measured [3] previously. The corresponding pK_{R^+} value for (2d) was similarly determined (see Experimental

TABLE 1

Effect of acid strength on rate constants for pentafulvene formation [a]

Cation	pK_{R^+} [b]	[HCl]/M	k_ψ/s^{-1} [c]	k_2/s^{-1} [d]
(2a)	−0.18	0.10	1.91×10^{-3}	2.88×10^{-2}
		0.30	5.33×10^{-3}	2.68×10^{-2}
		0.50	9.29×10^{-3}	2.81×10^{-2}
(2b)	0.68	0.10	2.70×10^{-3}	5.67×10^{-3}
		0.30	4.93×10^{-3}	3.45×10^{-3}
		0.50	5.93×10^{-3}	2.49×10^{-3}
(2c)	1.90	0.10	1.47×10^{-3}	1.85×10^{-4}
		0.30	1.82×10^{-3}	7.64×10^{-5}
		0.50	1.96×10^{-3}	4.94×10^{-5}
(2d)	−0.54 [e]	0.10	1.15×10^{-3}	3.99×10^{-2}
		0.30	2.03×10^{-3}	2.35×10^{-2}
		0.50	3.51×10^{-3}	2.44×10^{-2}

[a] At 27.5 °C in H_2O–MeCN (1 : 1 w/w). [b] Values from ref. 3 unless indicated otherwise. [c] Average values. [d] Assuming $k_2 = k_\psi K_{\mathrm{R}^+}/[\mathrm{HCl}]$. [e] This study.

TABLE 2

Effect of added salt on rate constants for pentafulvene formation [a]

Cation	pK_{R^+} [b]	[$NaClO_4$]/M	k_ψ/s^{-1} [c]	k_2/s^{-1} [d]	$(k_2)_{\mathrm{rel}}$ [e]
(2a)	−0.18	0.00	1.91×10^{-3}	2.88×10^{-2}	1.00
	0.47	0.50	6.99×10^{-3}	2.37×10^{-2}	0.82
	0.98	1.00	1.42×10^{-2}	4.19×10^{-2}	0.52
(2b)	0.68	0.00	2.70×10^{-3}	5.67×10^{-3}	1.00
	2.06	0.50	5.02×10^{-3}	4.34×10^{-4}	0.08
	2.70	1.00	5.87×10^{-3}	1.18×10^{-4}	0.02
(2c)	1.90	0.00	1.47×10^{-3}	1.85×10^{-4}	1.00
	3.34	0.50	1.66×10^{-3}	7.52×10^{-6}	0.04
	3.57	1.00	1.89×10^{-3}	5.08×10^{-6}	0.03

[a] At 27.5 °C in H_2O–MeCN (1 : 1 w/w) containing 0.01M-HCl. [b] See Experimental section. [c,d] As Table 1. [e] Relative k_2 values.

section). Since $k_2 \ll k_1$ (see later), the overall reaction approximates to a system in which pentafulvene (3) results by depletion of an alcohol (1)–carbocation (2) mixture whose composition, determined by the acid strength, is maintained close to an equilibrium value. Assuming such pre-equilibrium conditions, equations (2) and (3) can be derived. The k_2 values calculated from equation (3) are in Table 1.

$$k_\psi = [\mathrm{H}^+]k_{-1}k_2/k_1 \tag{2}$$

$$k_2 = k_\psi K_{\mathrm{R}^+}/[\mathrm{H}^+] \tag{3}$$

The effect of added salt on rates was studied for decomposition of the cations (2a—c) in H_2O-MeCN-0.1M-HCl containing $NaClO_4$ at various molarities. Again first-order kinetic behaviour was observed. We were unable to study a range of salts since most either cause separation of the mixed solvent or precipitation of the organometallic complex. Since the k_1 and k_{-1} values [equation (1)] for ferrocenylcarbocations are affected by the presence of inorganic salts,[11a] the pK_{R^+} values for (2a—c) in the same solvent containing HCl and $NaClO_4$ at appropriate molarities were measured (see Experimental section). From these values and the observed rate constants (k_ψ), the k_2 values were calculated from equation (3) as before. These results are in Table 2.

TABLE 3

Comparison of rate constants for fragmentation and nucleophilic addition [a]

Cation	pK_{R^+} [b]	k'_2/s^{-1} [c]	$(k'_2)_{\mathrm{rel}}$ [d]	k_1/s^{-1} [e]
(2a)	−0.18	3.05×10^{-2}	77	0.90
(2b)	0.68	8.91×10^{-3}	23	0.46
(2c)	1.90	3.94×10^{-4}	1	0.20
(2d)	−0.54	7.64×10^{-2}	194	

[a] In H_2O-MeCN (1 : 1 w/w) in the absence of acid. [b] From Table 1. [c] Values obtained by extrapolation of the k_2 values in the presence of HCl (Table 1) to zero acid concentration. [d] Relative k_2' values. [e] Values from ref. 3.

DISCUSSION

The rate constants (k_1) for addition of water to the cations (2a—c) in H_2O-MeCN in the absence of acid have been determined[3] earlier. The corresponding rate constants (k_2) for cation fragmentation, however, relate to reactions in the presence of HCl and it is clear from the results obtained (Table 1) that the k_2 value is sensitive to the presence of acid and to change in acid strength, particularly for the cations (2b and c). In order to permit meaningful comparison of k_1 and k_2 for each cation, k_2 values extrapolated to zero acid concentration were estimated from log k_2–[HCl] plots. These extrapolated rate constants (k'_2) and the corresponding k_1 values are in Table 3. For each cation for which direct comparison is possible, $k_1 \gg k'_2$ such that reaction in acid-free aqueous acetonitrile leads almost exclusively to alcohol product, as found experimentally.[3] As expected, increase in carbocation stability (*cf.* pK_{R^+} values) is accompanied by a reduction in the rate constants both for nucleophilic addition (k_1) and for fragmentation (k'_2). For the latter reaction, which is the more sensitive to change in carbocation stability [see $(k'_2)_{\mathrm{rel}}$ values; Table 3], there is an approximately linear relationship between $-\log k'_2$ and pK_{R^+}; *viz.* $-\log k'_2 = 0.9\mathrm{p}K_{\mathrm{R}^+} + 1.6$.

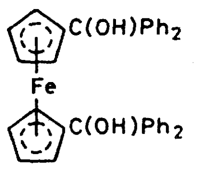
Previous work[11a] has shown that k_1 for addition of water to ferrocenylcarbocations is modestly depressed in the presence of mineral acid. As indicated earlier, a similar effect is apparent in the k_2 values (Table 1) for the cations (2b and c). The rate constants for fragmentation of the less stable carbocations (2a and d) are less sensitive to the presence of HCl within the range of concentrations used. For each of the kinetic experiments in H_2O–MeCN–HCl, however, the difference in the magnitudes of k_1 and k_2 for reaction of cation by the alternative pathways is sufficiently large to ensure that the earlier assumption of pre-equilibrium conditions is reasonable.

The sensitivity of the k_2 values to the concentration of HCl in the solvent reflects the importance of the ionic strength of the medium in determining the rates of reactions of carbocations in solution. This effect is further illustrated by the results of the kinetic experiments conducted in the presence of $NaClO_4$. Anions of low charge density, such as ClO_4^-, are particularly effective in stabilising a carbocation relative to the transition state for addition of water.[11] The resulting reduction in the k_1 value is accompanied by an increase in the corresponding k_{-1} value [see equation (1)] for acid-promoted alcohol heterolysis, such that the pK_{R^+} value becomes more positive upon addition of salt, as shown by the results in Table 2. Fragmentation of the cations (2a—c) into the pentafulvenes (3a—c) is likewise retarded in the presence of $NaClO_4$ as shown by the $(k_2)_{rel}$ values (Table 2). Again, the more stable carbocations (2b and c) show much greater sensitivity to increase in ionic strength than that exhibited by (2a).

Spontaneous scission of the metal–pentafulvene bond of tertiary ferrocenylcarbocations in aqueous acidic media is not a general reaction. Thus, dialkyl (*e.g.* $Fc\overset{+}{C}Me_2$) and alkylaryl (*e.g.* $Fc\overset{+}{C}MePh$) systems appear not to undergo this reaction. Neither is the propensity towards fragmentation at all related to carbocation stability as represented by pK_{R^+} values,[12] given * in parentheses; whereas $Fc\overset{+}{C}Ph_2$ (0.72) and $Fc_3\overset{+}{C}$ (5.77) fragment readily,[2,4a] $Fc\overset{+}{C}H_2$ (−1.28), $Fc\overset{+}{C}HPh$ (0.49), and $Fc_2\overset{+}{C}H$ (4.08) do not undergo spontaneous pentafulvene ligand loss. Relief of steric crowding upon fragmentation may be an important factor. In carbocations of the type (2), the aryl rings are forced to adopt a propellor-like conformation (*cf.* $Ph_3\overset{+}{C}$ [13]) which causes steric repulsion between these groups and the unsubstituted cyclopentadienyl ring. This interaction becomes progressively much more severe during torsion around the $Fc-(\overset{+}{C}Ar_2)$ bond, a process which is known [14] to occur with other ferrocenylcarbocations.

However, other factors besides steric must also be important. For example, we found no fragmentation of the sterically congested cation $Fc_2\overset{+}{C}Ph$ under reaction conditions which cause ready fragmentation of the cations (2). Under similar conditions, $Fc_2\overset{+}{C}Me$ does very slowly afford 6-ferrocenyl-6-methylpentafulvene but deprotonation of the methyl group is the predominant reaction when this cation is consumed in nucleophilic media. For a given ferrocenylcarbocation, resistance to fragmentation in aqueous acidic media may be provided both by internal (*i.e.* intrinsic metal–ligand bond strength) and external (*e.g.* cation solvation and/or ion-pairing) factors, or may result as a consequence of a very much larger k_1/k_2 partitioning ratio [see equation (1)] compared with those for cations of the type (2).

The fragmentation reaction is not restricted to monohydroxyalkylferrocenes. The diol (4) also fragments cleanly in aqueous acidic acetonitrile affording the pentafulvene (3a) which is formed from both ligands as shown by the product yield. The reaction probably occurs by prior formation of the carbocation (5).[15] Unfortunately, since solutions of (4) in CF_3CO_2H gave very poorly resolved ^1H n.m.r. spectra, we were unable to identify (5) or the carbodication[16] resulting from further dehydroxylation.



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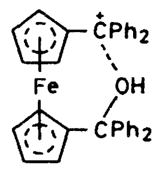

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EXPERIMENTAL

For general details, see Part 4.[14]

Preparation of Alcohols.—The alcohols (1a),[17] (1b),[3] (1d), (4),[18] and $Fc_2C(OH)Ph$ [19] were prepared by the addition of phenyl-lithium to the appropriate ketones, (1c) [3] by the addition of *p*-methoxyphenylmagnesium bromide to *p*-methoxybenzoylferrocene, and $Fc_2C(OH)Me$ [20] by the addition of methyl-lithium to diferrocenyl ketone. The required ketones were prepared by standard Friedel–Crafts reactions between ferrocene and the appropriate acyl chloride in CH_2Cl_2 in the presence of Al_2Cl_6. General experimental procedures for these reactions have been fully described [14] previously. Physical and spectroscopic properties of all of the known compounds were in accord with expectation. The new *alcohol* (1d) was obtained as a yellow solid, m.p. 125—126° (Found: C, 66.4; H, 4.5. $C_{24}H_{19}F_3FeO$ requires C, 66.1; H, 4.4%); $\tau(CDCl_3)$ 2.4—2.8 (9 H, m, aryl), 5.6—5.75 and 5.9—6.0 (2 H and 2 H, 2m, C_5H_4), 5.8 (5 H, s, C_5H_5), and 6.3br (1 H, s, OH).

Isolation of Pentafulvenes.—The following experiment is representative. Aqueous HCl (0.25M, 10 ml) was added to a solution of the alcohol (1a) (100 mg) in acetonitrile (10 ml). The resulting solution, containing the blue cation (2a), was allowed to stand in air overnight to ensure complete reaction. The solution, which was then orange, was neutralised by addition of aqueous NaOH and extracted with ether. The extract was washed thoroughly with water, diluted with light petroleum, dried ($MgSO_4$), and evaporated, and the residue was chromatographed on preparative thin-layer plates (SiO_2) using light petroleum as eluant. The pentafulvene (3a) (39 mg, 62%), which moved as an orange-red band, was recovered as a red solid, m.p. 79—80°, identical with an authentic sample [7] prepared by base-catalysed condensation of benzophenone and cyclopentadiene. The yield of product was not significantly affected when the reaction was carried out in the dark, or under nitrogen in oxygen-free solvent.

The pentafulvenes (3b—d) were similarly obtained by decomposition of the corresponding alcohols (1b—d). The physical and spectroscopic properties of (3b and c) were identical with reported data.[7] The pentafulvene (3d), which was not purified to analytical standard, was identified spectroscopically, $\tau(CDCl_3)$ 2.3—3.2 (9 H, m, aryl), 3.35—3.5, and 3.65—3.9 (2 H and 2 H, 2m, vinyl).

Investigation of Other Products.—In the preceding pentafulvene-forming reactions, there was no trace of ferrocene in the organic product. The aqueous solutions remaining after

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* The pK_{R^+} values relate to equilibria in water as the standard state; the corresponding values for solutions in aqueous acetonitrile are appreciably more negative.[3]

extraction of organic material contained neither ferricenium cation nor $[CpFe(NCMe)_3]^+$, but gave positive tests for ferrous and ferric ions.

When the decomposition of (1a) (100 mg) was carried out in a mixture of acetonitrile (15 ml), aqueous HCl (0.25M, 2 ml), and mesitylene (2 ml), as in the previous experiment, the pentafulvene (3a) was isolated as before but no trace of $[CpFe(\eta^6\text{-mesitylene})]^+$ was found in the aqueous solution.

When the decomposition of (1a) was similarly carried out in aqueous acidic acetonitrile containing an excess of 6,6-dimethylpentafulvene, the organic extract contained the product (3a) but no trace of neutral ferrocene derivatives derived from $Fc\overset{+}{C}Me_2$.

Rate Measurements.—Stock solutions (*ca*. 5×10^{-3}M) of the alcohols (1) in ethanol were prepared. Solutions of HCl at various molarities in H_2O–MeCN (1 : 1 w/w) were prepared by accurate dilutions with the same solvent of a standardised solution. *N.b.* Such solutions containing high acid concentrations (>0.5M) slowly develop acetic acid and freshly prepared solutions were used. The following general procedure was adopted.

The alcohol stock solution (*ca*. 30 µl) was added by microsyringe to H_2O–MeCN–HCl (*ca*. 3 ml) in a 1 cm cuvette with the same solvent in the reference beam. The spectrometer was locked on a suitable wavelength of maximum absorbance of the pentafulvene product (3) and the rate of growth of the absorbance was recorded. The reactions were followed to completion (no further spectral change). Good first-order $\ln(A_\infty - A_t)$ *versus* t rate plots were obtained and pseudo-first-order rate constants (k_ψ) were calculated conventionally using a least-squares best-fit computer program. Correlation coefficients better than 0.999 were obtained and duplicate runs gave acceptable agreement. The results are in Table 1.

Similar experiments were carried out in which the rate of disappearance of carbocation (2) was followed at a suitable wavelength of maximum absorbance. Good agreement was found between the k_ψ values thereby obtained and corresponding values determined earlier for pentafulvene formation. A series of related kinetic experiments was carried out using H_2SO_4 in place of HCl in the same mixed solvent. The calculated k_ψ values [5] were within *ca*. 10% of those found for reactions in the presence of HCl at the same molarities. The rates of fragmentation of the cations (2a—c) into the pentafulvenes (3a—c) in H_2O–MeCN (1 : 1 w/w) containing HCl (0.10M) and $NaClO_4$ (0.5 and 1.0M) were measured similarly and the k_ψ values are in Table 2.

The wavelengths (nm) of maximum absorbance of the carbocations and pentafulvenes, which were used for these rate studies, were as follows: (2a), 550; (2b), 440; (2c), 430; (2d), 600; (3a), 325; (3b), 340; (3c), 355; and (3d), 305.

pK_{R^+} *Measurements*.—The following general procedure was used. A stock solution (*ca*. 5×10^{-2}M, 50 µl) of the alcohol (1) in ethanol was diluted to 3 ml with a standardised solution of HCl in H_2O–MeCN (1 : 1 w/w) and the absorbance of the solution at a wavelength of maximum carbocation (2) absorbance was recorded immediately. From the rate of decay of this absorbance (due to pentafulvene formation), the absorbance at zero time was obtained by extrapolation. The $[R^+]/[ROH]$ equilibrium ratio was then calculated from the measured absorbances at the same wavelength of equimolar solutions in the same solvent containing 100% R^+ (concentrated acid) and 100% ROH (no acid), assuming the Beer–Lambert law. For each system, the procedure was repeated for a range of acid concentrations chosen to give $[R^+]/[ROH]$ equilibrium ratios covering the range 0.1—10. The pK_{R^+} values were then obtained as described [3] previously from $\log([R^+]/[ROH])$ *versus* H_R^{Fc} plots, which were linear with slopes close to unity. These values relate to water as the standard state; [3] the corresponding values for equilibria in H_2O–MeCN (1 : 1 w/w) are 0.9 log unit more negative. The results are in Table 1.

The pK_{R^+} values for (2a—c) were redetermined for solutions in the mixed solvent containing HCl (various molarities) and $NaClO_4$ (0.5 and 1.0M), using the same procedure. The results are in Table 2.

Properties of Carbocation Salts.—The BF_4^- salts of the cations (2a—c) were prepared by treatment of the alcohols (1a—c) in ice-cold acetic anhydride–ether with 45% aqueous HBF_4, following Allenmark's method.[6] The ClO_4^- salts were obtained similarly using $HClO_4$. Salts of (2a) were blue, and of (2b and c) green. These were stable for several weeks in the solid state in the absence of light; solutions in MeCN or halogenoalkanes, *e.g.* $(CH_2Cl)_2$, were stable for several hours in the dark. Treatment of freshly prepared solutions in MeCN with an excess of aqueous NaOH gave quantitative yields of the corresponding alcohols (1a—c). With NaOMe in methanol, the corresponding methyl ethers resulted. These were identified spectroscopically but were not purified to analytical standard.

Solutions of the alcohols (1) in CF_3CO_2H gave ^1H n.m.r. spectra characteristic of the corresponding carbocations (2): (2a), τ 2.0—2.8 (10 H, m, Ph), 3.4 and 4.6 (2 H and 2 H, 2t, C_5H_4), and 5.1 (5 H, s, C_5H_5); (2b), τ 2.1—3.1 (9 H, m, aryl), 3.5 and 4.7 (2 H and 2 H, 2m, C_5H_4), 5.25 (5 H, s, C_5H_5), and 6.0 (3 H, s, OMe); (2c), τ 2.1—3.1 (8 H, A_2B_2 pattern, aryl), 3.7 and 4.5 (2 H and 2 H, 2m, C_5H_4), 5.28 (5 H, s, C_5H_5), and 5.98 (6 H, s, OMe); (2d), τ 2.1—2.75 (9 H, m, aryl), 3.4, 4.6, and 4.8 (2 H, 1 H, and 1 H, 3m, C_5H_4), and 5.1 (5 H, s, C_5H_5).

Properties of Diferrocenylalkyl Cations.—(a) The alcohol $Fc_2C(OH)Ph$ (100 mg) was dissolved in aqueous acidic MeCN (500 ml, *ca*. 10^{-2}M in HCl). The solution, which contained the deep blue cation $Fc_2\overset{+}{C}Ph$, was left at room temperature for two days. The solution was then neutralised and the organic product was extracted with ether. Only the starting alcohol was recovered.

(b) Treatment of the alcohol $Fc_2C(OH)Me$ with aqueous acidic MeCN as in the preceding experiment gave the blue cation $Fc_2\overset{+}{C}Me$. After 15 h, the reaction was worked-up as before giving a mixture of ferrocene derivatives including 6-ferrocenyl-6-methylpentafulvene [21] which was identified from its characteristic ^1H n.m.r. spectrum, $\tau(CDCl_3)$ 3.2—3.7 (4 H, m, vinyl), 5.4 and 5.55 (2 H and 2 H, 2t, C_5H_4), 5.9 (5 H, s, C_5H_5), and 7.45 (3 H, s, Me).

Fragmentation of the Diol (4).—A solution of the diol (4) (200 mg) in acetonitrile (5 ml) was added to aqueous acetonitrile (1 : 1 w/w; *ca*. 150 ml) containing HCl (*ca*. 1M). The resulting deep green solution slowly became yellow-brown. After 3 h, the solution was diluted with water, then neutralised (aqueous NaOH), and the organic product was extracted with CH_2Cl_2. This was almost pure 6,6-diphenylpentafulvene (113 mg, 64%) which was identified by comparison with an authentic sample.

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