Nucleophilic Displacement of Hydroxyl by Cyanide Ion: Evidence for Neighbouring Group Participation in the Hydrolysis of a Ferrocenylmethyl Cyanide

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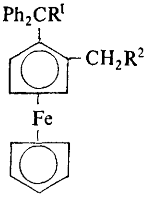
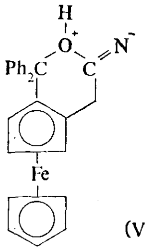
As part of an investigation of the nucleophilic substitutions of some 1,2-disubstituted ferrocenes,[1] we examined the reaction of 2-(hydroxydiphenylmethyl)ferrocenylmethyltrimethylammonium iodide (I)[1a] with potassium cyanide. In aqueous solution the expected hydroxy-cyanide (IIa) was obtained[1a] whilst in aqueous ethanolic solution the only isolable product was the cyano-amide (IIIa), m.p. 235·5—237° (69%), as evidenced by its elemental analysis and absorption spectra. Heating the hydroxy-cyanide (IIa) under reflux with aqueous ethanolic potassium cyanide afforded the cyano-amide (IIIa) (57%) and confirmed that the former compound was the intermediate in the formation of the latter. Also, the quaternary salt (IV)[1b] gave the amide (IIIa) (36%) with aqueous-ethanolic potassium cyanide The same reagents did not react with either ferrocenylmethylcyanide[2] or the diol (V)[1a] in separate experiments. The source of cyanide in the conversion of (II) into (III) was shown to be inorganic by the incorporation of radioactive cyanide into the product (IIIc), when the hydroxy-cyanide (IIa) was treated with aqueous ethanolic $K^{14}CN$. Similar levels of radioactivity were observed when the methiodide (I) was converted to the labelled cyanide (IIb) and then to the amide (IIIb).

One possible explanation of these results is that the hydrolysis of the cyanide (IIa) is assisted by intramolecular addition of the hydroxy-group to the cyanide group. This leads, presumably through attack by cyanide ion at the diphenyl-substituted carbon atom of the oxonium intermediate (VI), to the amide (IIIa). Neighbouring group participation in cyanide hydrolysis has not previously been reported.

The critical dependence of product upon solvent may be due, in part, to the solubility of both the methiodide (I) and the cyanide (II) in aqueous ethanol and their insolubility in water.





(VI)

	R^1	R^2
(I)	OH	$N^+Me_3I^-$
(IIa)	OH	CN
(IIb)	OH	$\overset{*}{C}N$
(IIIa)	CN	$CONH_2$
(IIIb)	CN	$\overset{*}{C}ONH_2$
(IIIc)	$\overset{*}{C}N$	$CONH_2$
(IV)	OH	$N^+(CH_2)_4MeI^-$
(V)	OH	OH

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[1] (a) D. W. Slocum, B. W. Rockett, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1965, **87**, 1241; (b) M. Hadlington, B. W. Rockett, and A. G. Nelhans, *J. Chem. Soc.* (*C*), 1967, 1436; G. Marr, R. E. Moore, and B. W. Rockett, *J. Chem. Soc.* (C), in the press.

[2] C. R. Hauser, J. K. Lindsay, D. Lednicer, and C. E. Cain, *J. Org. Chem.*, 1957, **22**, 717.