Enigmatic Reactions of α-Ferrocenyl Cations in Sulphuric Acid[1]

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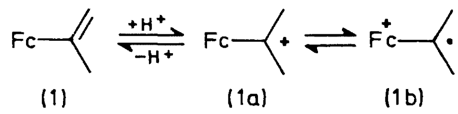
Summary αα-Dimethyl-α-ferrocenyl cation in sulphuric acid does not form 2,3-diferrocenyl-2,3-dimethylbutane as previously reported, but on quenching affords diferrocenyl-olefins, which on protonation in sulphuric acid undergo reduction to diferrocenyl-alkanes.

THE stability of α-ferrocenyl cations is beyond question.[2] Indeed, solutions of 2-ferrocenylpropene (1) in sulphuric acid† are remarkably stable and after many days the n.m.r. spectrum of the cation (1a) is unchanged.[3] Hence it is surprising to find a claim[4] for the synthesis of 2,3-diferrocenyl-2,3-dimethylbutane (2) by the dimerisation of this ion (1a), *via* the radical cation (1b), in sulphuric acid. In a reinvestigation of this reaction we have found no evidence for the formation of this compound.

The products after work-up, in addition to regenerated 2-ferrocenylpropene and 2-ferrocenylpropan-2-ol, are the



Equation 1

(2)

isomeric diferrocenyl-olefins (3a) m.p. 89—93°, and (4a) m.p. 88°.[5]‡§ There is no evidence to suggest that these

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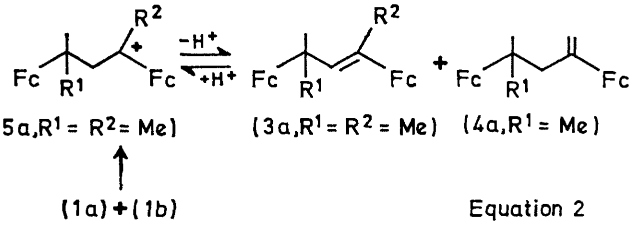
† The sulphuric acid (98%) used throughout was AnalaR supplied by B.D.H., Ltd.

‡ The symmetric dimer [(2) m.p. 215–216°, n.m.r. ($CDCl_3$, τ), ferrocenyl protons 5·98(s), 6·03(m), and 6·23 (m), alkyl protons 8·83(s)][6] was prepared from 2-ferrocenylpropane by zinc–acetic acid–HBr reduction.[7]

§ Of the three previous claims for the synthesis of 2,3-diferrocenyl-2,3-dimethylbutane two of the "products" reported are presumably either a mixture of olefins (3a and 4a)[3] or one of the isomers (3a)[5] (see ref. 8).

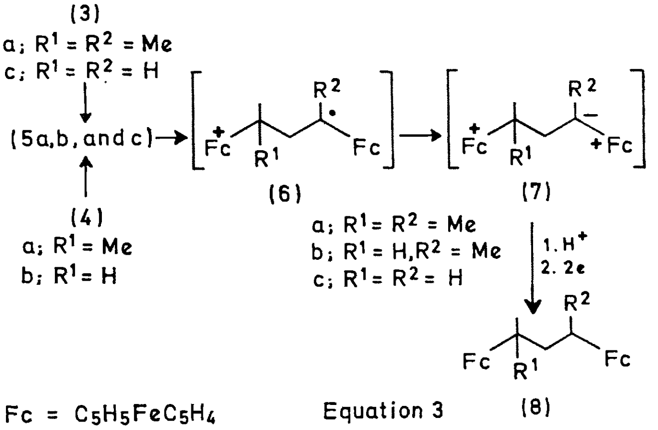
olefins are formed in sulphuric acid (*vide* the n.m.r. spectrum).[3] We believe they are the result of alkylation of 2-ferrocenylpropene by cation (1a) during the quenching of the sulphuric acid solution (Equation 2). By selection of the quenching conditions, the dimer ratio (3a : 4a) can be altered. The kinetic product (4a) (28·3%) is obtained by quenching on ice, while quenching in water gives an approximately equal amount of (3a) and (4a) (66·4%). If the temperature of the aqueous phase is allowed to rise above 70° during quenching, cyclic products formed by dilute acid cyclisation of (3a) and (4a) are the major products.



Equation 2

Solutions of 2-ferrocenylpropan-2-ol in strong acid also form the cation (1a).[8] On work-up of a sulphuric acid solution of the carbinol under our conditions another new product (8a) m.p. 78—79°, in addition to the previously mentioned olefins, was isolated. This reaction is, to some extent, temperature-dependent, the yield of alkane (8a) increasing with temperature. The formation of the olefins (3a) and (4a) takes place during quenching, but the alkane (8a) must be formed *in situ*. It would appear that the genesis of this compound involves the alkylation of 2-ferrocenylpropene by cation (1a). This alkylation only occurs in dilute acid, thus the transient dilution of the solvating sulphuric acid during the dissolution of 2-ferrocenylpropan-2-ol must allow the local acidity to drop to the correct value for the equilibrium (Equation 1) to occur and alkylation to take place. Cation (5a) resulting from this alkylation must be the precursor of the alkane.

Several 1,3-diferrocenyl-olefins undergo this reduction in sulphuric acid. Dissolution of (4a) or a 1 : 1 mixture of (3a) and (4a) gave a blue-green solution which did not exhibit an n.m.r. spectrum, suggesting the presence of paramagnetic species.¶ No e.s.r. spectrum was obtained. Quenching of the acid solution in water gave a blue-green phase which after reduction (ascorbic acid) afforded the alkane (8a) (87·5%). Similarly, olefins (4b) and (3b) are reduced efficiently in sulphuric acid to the alkanes (8b) (97·7%; a mixture of diastereoisomers) and (8c) (57·7%), respectively. The above examples involve the formation of the cation (5) by protonation of an olefin; however, an alternative route *via* the alcohol (8; R^1 = H, R^2 = OH) also affords the alkane (8c) (82.9%). Cation (5) is thought to undergo two one-electron-transfer processes (5) → (6), (6) → (7), (Equation 3) enabling the reduction to occur by a second protonation step. The second one-electron-transfer is suggested by the fact that no dimeric products arising from dimerization of the radical-cation (6)** were detected—hence its transience. Also (1a) being inert in sulphuric acid and (5) which contains two ferrocenyl groups undergoing reduction, suggests participation by both iron atoms and possibly that the ferrocenyl moiety not attached to the cationic centre is the initial electron donor. The paramagnetism then results from the ferricinium form of (8). Further evidence for the above scheme is at present being sought.



Fc = $C_5H_5FeC_5H_4$

Equation 3

All new compounds described had satisfactory analytical figures and spectral properties in accord with the structures assigned.

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¶ It is well known that the presence of paramagnetic species broadens and even suppresses n.m.r. signals.

** α-Ferrocenyl cations can readily be reduced by zinc in acetic acid[7] to afford a ferrocenylcarbinyl radical, which dimerises. Intramolecular electron transfer in non-deprotonatable α-ferrocenyl cations is the mechanism suggested in explanation of the formation of 1,2-diferrocenyl-ethanes from the corresponding carbonium ions in strong acid. (See D. E. Bublitz and K. L. Rinehart, *Org. Reactions*, 1969, **17**, 1).

[1] Previous paper: see W. M. Horspool, R. G. Sutherland, and B. J. Thomson, submitted to *J. Chem. Soc.* (*C*).

[2] M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

[3] W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1967, 768.

[4] K. L. Rinehart, P. A. Kittle, and A. F. Ellis, *J. Amer. Chem. Soc.*, 1960, **82**, 2082.

[5] A. Wende and H. J. Lorkowski, *Plaste und Kautschuk*, 1963, **10**, 32.

[6] A compound (m.p. 203—205) has been reported by W. P. Fitzgerald (*Diss. Abs.*, 1964, **24**, 2687). The evidence for its identity as the symmetric dimer (2) was based solely on the i.r. spectrum.

[7] M. Cais and A. Eisenstadt, *J. Org. Chem.*, 1965, **30**, 1148. These authors first described this method for the synthesis of other symmetrical dimers.

[8] J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, 1969, **91**, 4324.