Rearrangements of Ferrocenylcarbonium Ions by a Novel Inter-cation Exchange Mechanism

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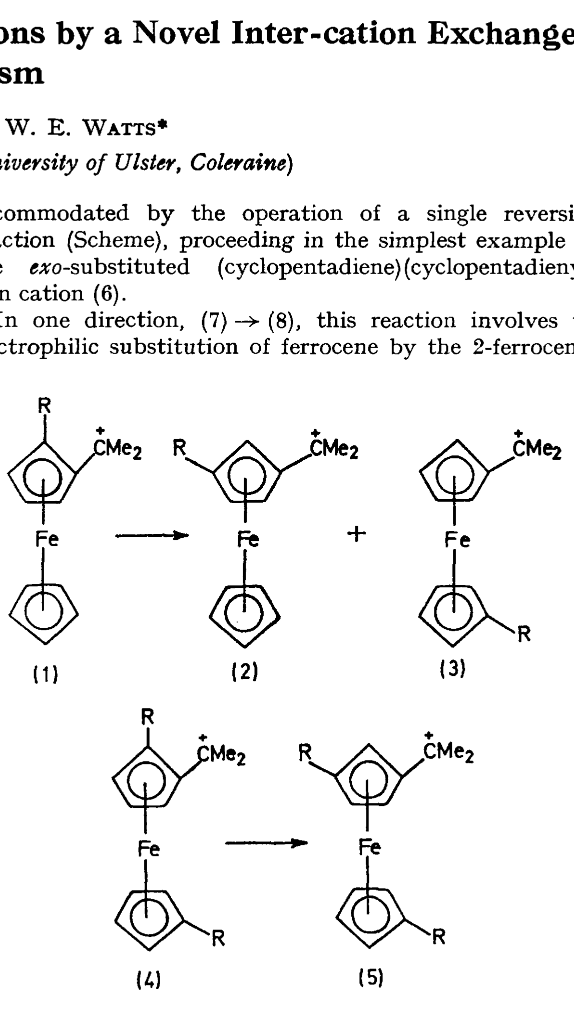
Summary In CF_3CO_2H solution, α-substituted 2-ferrocenyl-2-propyl cations rearrange to a mixture of the isomeric β- and 1′-substituted cations in the presence of catalytic amounts of ferrocene or an alkylferrocene, by means of an equilibrium-controlled transfer of the (Me_2C^+) group between cations, ferrocene or an alkyl derivative functioning as transport agent.

CONTROVERSY and speculation continue to surround the question of the structure of ferrocenylcarbonium ions and the factors responsible for their enhanced thermodynamic stability.[1] During an investigation of this problem, we have discovered a ready rearrangement of α-substituted 2-ferrocenyl-2-propyl cations (1; R = alkyl) to a mixture of the corresponding β- and 1′-substituted cations (2 and 3, respectively) in CF_3CO_2H solution. The related α,1′-disubstituted cations [4; R = alkyl or $(CH_2)_n$ (n = 3—5)] undergo a similar rearrangement, giving the β,1′-disubstituted isomers (5).

The progress of the rearrangements (1) → (2) + (3) and (4) → (5) can be followed conveniently by monitoring the growth or decay of the ^1H n.m.r. resonances associated with each species.† For example, the rearrangement of the α,1′-dimethyl cation to its β,1′-isomer (4 → 5; R = Me) is characterised by the gradual disappearance in the spectrum of the four methyl singlets of the precursor (4) at τ 7·60, 7·80 (Me_2C methyl groups), 8·03 (α-methyl group), and 8·24 (1′-methyl group) and their replacement by the four methyl singlets of the product (5) at τ 7·84, 7·86 (Me_2C methyl groups), 7·70 (β-methyl group), and 8·20 (1′-methyl group) ($SiMe_4$ internal standard).

The clue to the mechanism of these rearrangements was provided by the discovery that the transformations are markedly accelerated in the presence of catalytic amounts of an alkylferrocene or ferrocene itself. Indeed, using rigorously purified alcohol precursors and CF_3CO_2H solvent, α-substituted cations of the types (1) and (4) are stable and resist rearrangement. The experimental results can be accommodated by the operation of a single reversible reaction (Scheme), proceeding in the simplest example *via* the *exo*-substituted (cyclopentadiene)(cyclopentadienyl)-iron cation (6).

In one direction, (7) → (8), this reaction involves the electrophilic substitution of ferrocene by the 2-ferrocenyl-2-propyl cation. The pronounced reactivity of the ferrocene molecule towards even weak electrophiles is well documented[2] and a few examples of reactions of this nature have in fact been reported.[3] From steric considerations, addition of the bulky electrophile (7) to the *exo*-side of the ferrocene ring would be favoured, leading to the formation of the intermediate (6) with the stereochemistry depicted.



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† Generated from the corresponding alcohols ($-CMe_2OH$) in CF_3CO_2H.

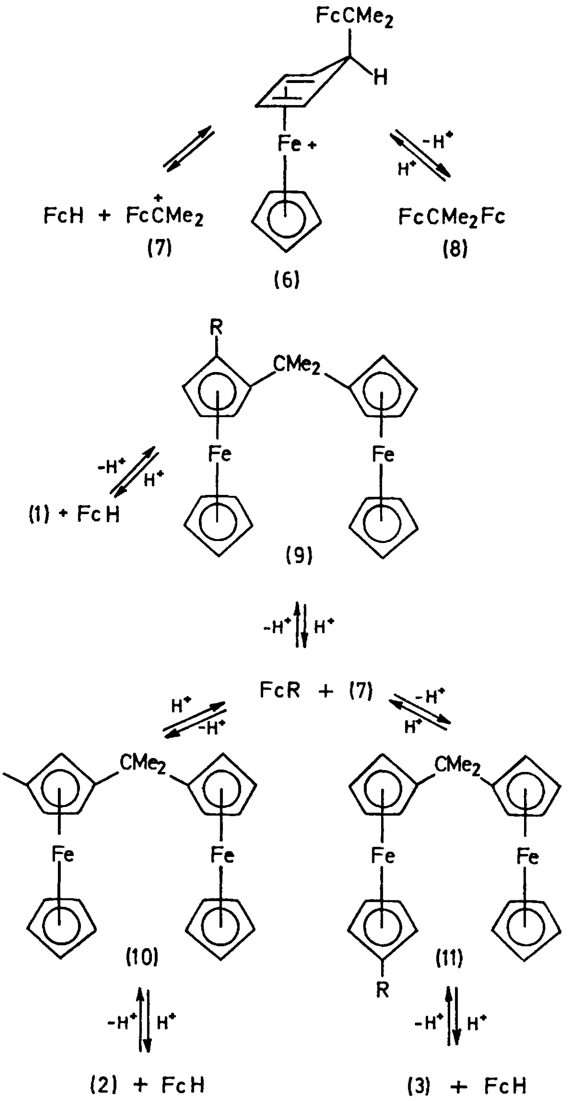
In the reverse direction, (8) → (7), the process involves the acid-promoted fragmentation of 2,2-diferrocenylpropane. We have independently verified that this reaction does occur smoothly and immediately when (8), prepared separately, is dissolved in CF_3CO_2H. Spectroscopic study (^1H n.m.r.) has shown that the position of equilibrium in the reaction (7) + FcH $\rightleftharpoons$ (8) + H^+ lies far the on side of the carbonium ion in CF_3CO_2H.

Fission of a carbon–carbon bond under such relatively mild conditions is remarkable and is clearly made possible by the exceptional stability of the carbonium ion produced [*cf.* a pK_{R+} value of $-0{\cdot}01$ has been measured[4] for the cation (7)]. Since it has been shown[5] previously that the iron atom is the site of protonation in ferrocene itself, it appears probable that formation of the *exo*-substituted intermediate (6) from (8) would occur by the so-called "ricochet" mechanism,[6] involving transfer of a proton to the *endo*-side of the cyclopentadienyl ring from the iron atom, its original location.‡

Ferrocene is depicted as the initiator in the Scheme although any alkylferrocene would serve the same function. Each reversible reaction indicated is merely a variant of the basic reaction discussed previously, modified by the presence of an alkyl substituent in the ferrocene rings. Under thermodynamic control, the final equilibrium mixture produced in each case therefore reflects the relative thermodynamic stabilities of the participating carbonium ions (1), (2), and (3). Maximum resonance stabilisation of a carbonium-ion centre by a ferrocenyl group is achieved when the cyclopentadienyl–C^+R_2 ligand can achieve a planar geometry, thereby allowing maximum p_π–p_π conjugation. The α-substituted cations (1), however, are destabilised in such a conformation by steric repulsion between the alkyl substituent R and the proximate methyl group of the (Me_2C^+) substituent. In consequence, the relative concentration of the α-substituted cation in the final equilibrium mixture is below the level of detection by ^1H n.m.r. spectroscopy.

Similarly, the relative equilibrium concentrations of the diferrocenylpropanes (9), (10), and (11) are too low for detection (*vide supra*) while the amount of the parent cation (7) produced is determined by the amount of ferrocene originally present. In principle and in practice, only trace amounts of initiator are required although it is obvious that the *rate* at which equilibrium between the cations is established will be dependent upon the initial concentration of the initiator. At low concentrations, however, all that is observed spectroscopically starting with an α-substituted cation (1) is a gradual rearrangement to the β- and 1′-isomers (2) and (3), respectively.

The rearrangement of the α,1′-disubstituted cations (4) can be explained by a similar equilibrium-controlled rearrangement. The presence of the second alkyl substituent simply renders indistinguishable the pathways leading to (2) and (3) in the Scheme such that a single rearrangement product (5) is formed.



Scheme[a,b]

[a] Fc = ferrocenyl throughout.

[b] In CF_3CO_2H solution, ferrocene and its alkyl derivatives undergo rapid proton-exchange with solvent.

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‡ However, see ref. 7.

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