Stable Carbonium Ions. Part VI.[1] Inter-cation Exchange Rearrangements of Ferrocenylalkylium Ions

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In $\mathrm{CF_3CO_2H}$ solution, α-substituted 1-ferrocenylethylium and 1-ferrocenyl-1-methylethylium cations rearrange to a mixture of the isomeric β- and 1′-substituted cations in the presence of ferrocene or an alkylferrocene, by means of an equilibrium controlled transfer of the ($\mathrm{Me\overset{+}{C}H}$) or ($\mathrm{Me_2C^+}$) group between cations, ferrocene, or an alkyl derivative functioning as transport agent. Ruthenocenylalkylium ions, and thermodynamically more stable ferrocenylalkylium ions (*e.g.* $\mathrm{Fc\overset{+}{C}HPh}$, $\mathrm{Fc_2\overset{+}{C}H}$) do not undergo similar rearrangements.

Ferrocenylalkylium ions ($\mathrm{Fc\overset{+}{C}R_2}$) are generated quantitatively when 1-hydroxyalkylferrocenes ($\mathrm{FcCR_2}$-OH) are dissolved in $\mathrm{CF_3CO_2H}$ and give rise to readily interpretable ^{1}H n.m.r. spectra in this solvent.[2] The simplicity and predictability of the proton resonance patterns of these spectra greatly facilitate investigation of the behaviour of the ions in solution and this technique has been used, for example, to study rotational isomerisation in the system.[3] During the course of this work, it was accidentally discovered [4] that 1-ferrocenyl-1-methylethylium cations bearing alkyl substituents at the α- and 1′-positions or containing an interannular α,1′-alkyl bridge (2) rearrange cleanly in $\mathrm{CF_3CO_2H}$ to give isomeric cations (3) in which the alkyl groups or bridging chain are located β, 1′- to the ($\mathrm{Me_2C^+}$) substituent. The ^{1}H n.m.r. spectra of these rearrangement products were indistinguishable from those of the β,1′-substituted cations, generated unambiguously from the alcohols (4), and were quite different from those of the original unstable cations (2) obtained from the α,1′-substituted alcohols (1) (see Table 1).

Although the spectroscopic evidence for the rearrangements (2) ⟶ (3) appeared conclusive, corroboration of the nature of the process was sought from a product study of a representative example. The α,1′-dimethyl cation (2a) was prepared by dissolution of the alcohol (1a) in $\mathrm{CF_3CO_2H}$. When complete rearrangement to the isomeric cation (3a) had been indicated (^{1}H n.m.r.), the solution was quenched with dilute aqueous base whereupon proton elimination occurred as the main reaction affording the isopropenyl derivative (5). Catalytic hydrogenation of this rather unstable alkene gave the isopropyl compound (6) which was identical with that obtained by mixed-hydride reduction [5] of the β,1′-substituted alcohol (4a). The physical and spectroscopic properties of this alkylferrocene (6) were clearly different from those of its isomer (7) which was prepared for comparison by reduction of the α,1′-substituted alcohol (1a). Since alcohols (1a) and (4a) had been prepared by addition of methyl-lithium to α- and β-acetyl-1,1′-dimethylferrocene respectively, whose structures are well established,[6] the course of the rearrangement (2a) ⟶ (3a) is beyond doubt.

It was first thought that the mechanism of these rearrangements probably involved an intra-ionic [1,2]

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[1] Part V, T. D. Turbitt and W. E. Watts, preceding paper.

[2] (*a*) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1966, 1695; W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1967, 786; M. Hisatome and K. Yamakawa, *Tetrahedron*, 1971, **27**, 2101; (*b*) J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **91**, 4324.

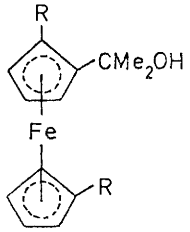
[3] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

[4] Preliminary communication; T. D. Turbitt and W. E. Watts, *J.C.S. Chem. Comm.*, 1972, 947.

[5] M. J. A. Habib and W. E. Watts, *J. Chem. Soc.* (*C*), 1969, 1469.

[6] K. L. Rinehart, K. L. Motz, and S. Moon, *J. Amer. Chem. Soc.*, 1957, **79**, 2749.

shift of either the (Me_2C^+) group or the α-alkyl substituent. In order to differentiate between these pathways, the αβ-dimethyl and αα′-dimethyl cations (8c) and (11c) respectively were prepared in the expectation that only one of these species would rearrange



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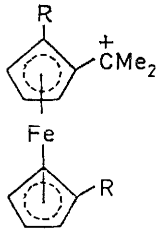

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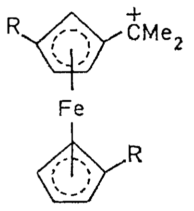

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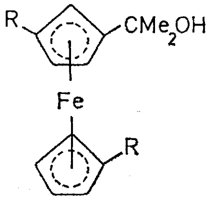
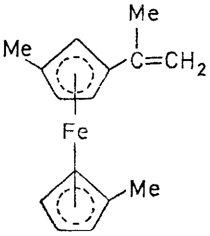


(4)

a; R = Me
b; R = Et
c; R = Pr^i
d; R = Bu^t
e; R,R = $[CH_2]_3$
f; R,R = $[CH_2]_4$
g; R,R = $[CH_2]_5$



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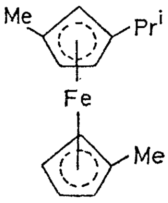

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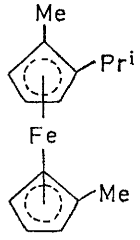


(7)

[*i.e.*, either (8c) ⟶ (9c) by (Me_2C^+) shift, or (11c) ⟶ (12c) by α-methyl shift] while the other would remain unchanged. The alcohol precursors of these cations were prepared by the following method. Friedel–Crafts acetylation of 1,2- and 1,3-dimethylferrocene gave, in each case, a mixture, difficult to separate, of the three possible monoacetyl derivatives (8a)—(10a) and (11a)—(13a) respectively whose structures could be assigned from their spectral characteristics (see Experimental section). Treatment of these ketones individually with methyl-lithium afforded the corresponding tertiary alcohols (8b)—(10b) and (11b)—(13b) which were converted quantitatively into the carbonium ions (8c)—(10c) and (11c)—(13c) in CF_3CO_2H. The characteristic ^1H n.m.r. spectra of these six isomeric cations are summarised in Table 1. After completion of this synthetic work, however, we were frustrated to discover that neither the αβ- nor the αα′-substituted cation (8c) and (11c) respectively underwent [1,2] rearrangement, even in hot CF_3CO_2H.

TABLE 1

^1H N.m.r. spectra of tertiary ferrocenylalkylium ions [a]

	Alkyl resonances (τ) [b]		Cyclopentadienyl resonances (τ) [b,c]		
Cation	(Me_2C^+)	Other substituents	α-H	β-H	1′-H
(2a)	7·60, 7·80(2s)	8·03, 8·24 (2s, Me)	5·30	3·95, 4·00	5·33
(2b)	7·57, 7·76 (2s)	8·78, 8·88 (2t, Et) [d]	5·30	3·85, 3·97	5·27
(2c)	7·54, 7·77 (2s)	8·78, 8·88 (2d, Pr^i) [e]	5·25	3·75, 4·00	5·15
(2d)	7·45, 7·73 (2s)	8·68, 8·84 (2s, Bu^t)	5·25	3·75	5·25
(2e)	7·57, 7·87 (2s)	7·5—7·3 (CH_2)	*f*	*f*	*f*
(2f)	7·50, 7·80 (2s)	7·0—8·4 (CH_2)	*f*	*f*	*f*
(2g)	7·61, 7·80 (2s)	7·6—8·4 (CH_2)	*f*	*f*	*f*
(3a)	7·84, 7·86 (2s)	7·70, 8·20 (2s, Me)	5·15	3·95	5·30
(3b)	7·86(s) [g]	8·67, 8·90 (2t, Et) [d]	5·30	3·95	5·30
(3c)	7·82(s) [g]	8·57, 8·67, 8·86 (3d, Pr^i)[e,h]	5·25	3·90	5·25
(3d)	7·89, 7·93 (2s)	8·65, 8·89 (2s, Bu^t)	5·00, 5·50	3·70	5·20
(3e)	7·72. 7·84 (2s)	7·55—8·15 (CH_2)	*f*	*f*	*f*
(3f)	7·80(s) [g]	7·0—8·3 (CH_2)	*f*	*f*	*f*
(3g)	7·83(s) [g]	7·0—8·4 (CH_2)	*f*	*f*	*f*
(8c)	7·52, 7·72 (2s)	7·81, 8·08 (2s, Me)	5·45(d)	3·95(d)	5·45(s)
(9c)	7·84(s)	7·74 (s, Me)	5·24(s)		5·36 (s)
(10c)	7·80(s)	8·23 (s, Me)	5·13(t)	3·97(t)	5·30
(11c)	7·50(s)	8·03 (s, Me)		3·96(s)	5·25
(12c)	7·58, 7·78 (2s)	7·78, 8·00 (2s, Me)	5·45(d)	3·84(d)	5·29(s)
(13c)	7·82(s)	8·20 (s, Me)	5·20(t)	3·86(t)	5·36
(14)	7·60, 7·80 (2s) [i]	8·03, 8·24 (2s, Me)	5·30	3·95, 4·00	5·33
(15)	7·84 ,7·86 (2s) [i]	7·70, 8·20 (2s, Me)	5·15	3·95	5·30
(16c)	7·53, 7·75 (2s)	8·00 (s, Me)	5·30	3·82, 3·89	5·19(s)
(17c)	7·76, 7·78 (2s)	7·70 (s, Me)	5·13, 5·25	3·80	5·23(s)
(18c)	7·80(s)	8·10 (s, Me)	5·10(t)	3·83(t)	5·27
(19c)	7·22, 7·40 (2s)	8·68 (s, Bu^t)	5·50	3·68, 4·00	5·17(s)
(20c)	7·80(s) [g]	8·62 (s, Bu^t)	5·15	3·75	5·17(s)
(21c)	7·79(s)	8·82 (s, Bu^t)	5·00(t)	3·63(t)	5·20(s)
(23)	7·77(s)		5·05(t)	3·72(t)	5·14(s)

[a] For CF_3CO_2H solutions with Me_4Si as internal reference. The spectrum of the 1-ruthenocenyl-1-methylethylium cation gives τ 3·83 (t, β-H), 4·63 (t, α-H), 4·74 (s, 1′-H), 7·72 (s, Me_2C^+); *cf.* spectrum of (23). [b] Integrated relative intensities of signals agreed with the proton assignments; multiplets unless indicated otherwise; (s) singlet, (d) doublet, (t) triplet, (q) quartet. [c] The location of the ring protons relative to the (Me_2C^+) substituent is indicated. [d] Methylene resonances appear in the range τ 7·0—8·2. [e] Methine resonances appear in the range τ 6·8—8·0. [f] Ring-proton resonances appear as a complex pattern in the range τ 3·6—5·6. [g] Individual methyl resonances not resolved. [h] The methyl groups of the isopropyl substituent attached to the fulvene ligand are magnetically non-equivalent. [i] Relative intensity of each singlet corresponds to 1·5H [*cf.* spectra of (2a) and (3a)] (see text).

The possibility of methyl scrambling in the rearrangement of the α,1′-dimethyl cation [(2a) ⟶ (3a)] was excluded by an investigation of a deuterium labelled system. In the conversion of the cation (14) into its isomer (15), it was established (^1H n.m.r.) that the CD_3 group is retained by the carbonium ion centre and does not exchange with either of the methyl groups attached to the rings. The straightforward method of preparation of the alcohol precursors of these labelled cations is given in the Experimental section.

In a further attempt to shed light upon the rearrange-

TABLE 2

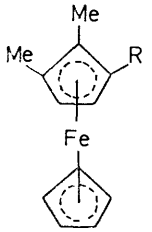
^{1}H N.m.r. spectra of secondary ferrocenylalkylium ions [a]

	Alkyl resonances (τ) [b]			Cyclopentadienyl resonances (τ) [b,c]		
Cation	HC$^+$	MeC$^+$	Other substituents	α-H	β-H	1′-H
(27a)	3·17(q)	7·58(d)	8·02, 8·13 (2s, Me)	5·95	3·93, 4·09	5·10br(s)
(27b) + (28b) [d]	3·06(q)	7·82(d)	7·62, 7·73, 8·08 (3s, Me)	5·15, 5·65, 5·81	3·88, 4·04	5·15br(s)
(27c)	2·99(q)	7·50(d)	7·96 (s, Me)	5·84	3·73, 3·96	4·94(s
(27d) + (28d) [d]	2·99(q)	7·82, 7·84 (2d)	7·64, 7·73 (2s, Me)	5·00, 5·64	3·70, 3·86	5·03(s)
(27e) ≡ (28e) [e]	2·92(q)	7·76(d)	8·11 (s, Me)	5·04, 5·57	3·76, 3·86	5·02br(s)
(28a)	2·84(q)	7·77(d)	8·13, 8·35 (2s, Me)	5·10	3·88, 4·04	5·10br(s)
(28c)	2·65(q)	7·72(d)	8·32 (s, Me)	5·05	3·73, 3·86	5·00(s)
$\mathrm{Fc}\overset{+}{\mathrm{C}}\mathrm{HMe}$	2·88(q)	7·75(d)		4·97, 5·51	3·64, 3·79	4·97(s)

[a] For CF_3CO_2H solutions with Me_4Si as internal reference. The spectrum of the 1-ruthenocenylethylium cation gives τ 3·72 (q, HC$^+$), 4·36 and 4·98 (2m, α-H), 3·72 and 3·82 (2m, β-H), 4·57 (s,1′-H), and 7·86 (d, MeC$^+$). [b,c] See Table 1. [d] Equimolar mixture of diastereoisomeric cations. [e] Equivalent structures.

ment mechanism, the behaviour of the α-methyl cation (16c) was studied. Using a synthetic approach similar to that previously adopted, the α-, β-, and 1′-acetyl derivatives[7] of methylferrocene (16a)—(18a) were converted into the tertiary alcohols (16b)—(18b) and thence into the isomeric carbonium ions (16c)—(18c). It was thereby found that the α-substituted cation (16c) rearranges to give not only the β-methyl cation (17c) but also approximately equal amounts of the 1′-methyl isomer (18c), an inter-ring migration apparently having occurred.

Other observations made at this time helped to clarify the situation. Certain samples of α-substituted alcohols [*e.g.* (1a)] were found to give CF_3CO_2H solutions in which rearrangement of the α-substituted cations proceeded either sluggishly or not at all. With this lead, it was then quickly found that the rearrangements (2) ⟶ (3) occur only in the presence of at least trace amounts of ferrocene or an alkylferrocene. Using rigorously purified alcohol precursors, the α-substituted cations (2a—g), (8c), (11c), (12c), (14), (16c), and (19c) are stable in CF_3CO_2H and resist rearrangement.



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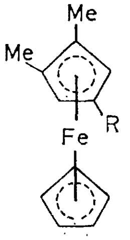

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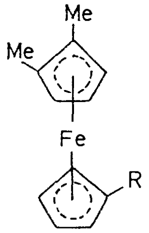

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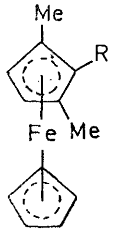

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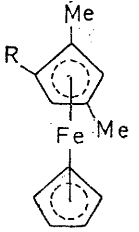

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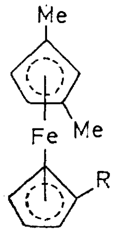
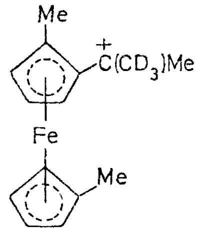


(13)

a; R = COMe
b; R = CMe_2OH
c; R = $\overset{+}{C}Me_2$



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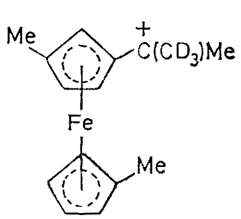

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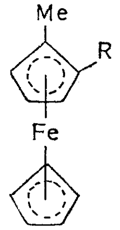

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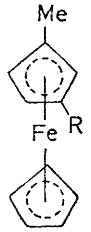

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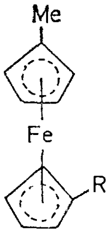

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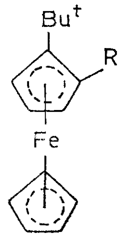

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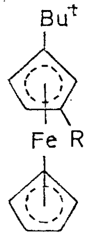

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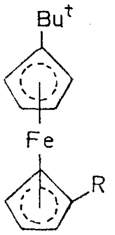

(21)

a; R = COMe
b; R = CMe_2OH
c; R = $\overset{+}{C}Me_2$

The final clue to the mechanism came from the observation that, in CF_3CO_2H, 2,2-diferrocenylpropane[8] (22) underwent immediate protonation followed by fragmentation to generate ferrocene and the 1-ferrocenyl-1-methylethylium cation (23). It was also found that, although the cyclopentadienyl ring protons of ferrocenylalkylium ions [*e.g.* (23)] do not undergo H–D exchange in CF_3CO_2D, fast exchange of the ring

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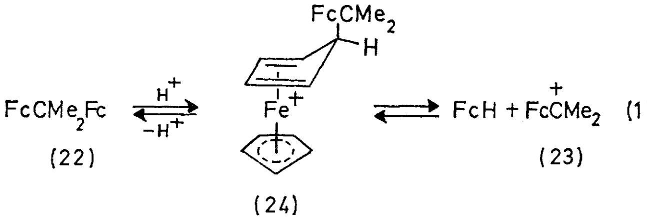
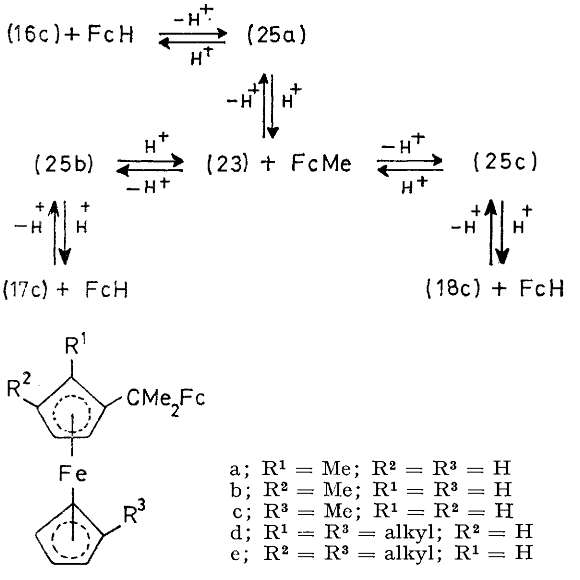
[7] R. A. Benkeser, Y. Nagai, and J. Hooz, *J. Amer. Chem. Soc.*, 1964, **86**, 3742.

[8] T. H. Barr, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, 1969, **25**, 6001.

protons of the cation (23) does occur in CF_3CO_2D containing ferrocene. Reversible protonation–deprotonation of ferrocene and its alkyl derivatives in strongly acidic solvents is well established although there are conflicting views of the mechanism of the process.[9,10] In the original reaction, therefore, it follows that the acid-promoted fragmentation of the diferrocenylalkane (22) to ferrocene and the cation (23) must be reversible. The ^1H n.m.r. spectrum of the mixture shows that the position of equilibrium lies far on the side of the cation in CF_3CO_2H.



(22) (24) (23)



(25)

a; $R^1 = Me$; $R^2 = R^3 = H$
b; $R^2 = Me$; $R^1 = R^3 = H$
c; $R^3 = Me$; $R^1 = R^2 = H$
d; $R^1 = R^3 =$ alkyl; $R^2 = H$
e; $R^2 = R^3 =$ alkyl; $R^1 = H$

SCHEME

The rearrangements can then be accommodated by the operation of a single reversible reaction proceeding in the simplest example *via* the (5-*exo*-substituted cyclopentadiene)cyclopentadienyliron cation (24) [equation (1)]. In one direction, this reaction involves the acid-promoted fragmentation of a diferrocenylalkane. Fission of a carbon–carbon bond under such relatively mild conditions is made possible by the basicity of the iron atom in ferrocene derivatives[9] and by the exceptional thermodynamic stability[1] of the ferrocenylalkylium ion produced. Formation of the intermediate (24) from (22) would occur by the so-called 'ricochet' mechanism,[11] involving transfer of a proton to the *endo*-side of the cyclopentadienyl ring from the iron atom, its original location. In the reverse direction, the process involves the electrophilic substitution of ferrocene by the cation (23). The high reactivity of the ferrocene molecule towards even weak electrophiles is well documented[12] and a few examples of reactions of this type have been reported.[13] From steric considerations, addition of the bulky electrophile to the *exo*-side of the cyclopentadienyl ring would be favoured, leading to the formation of the intermediate (24) with the stereochemistry shown.

As a representative example, the mechanism of rearrangement of the α-methyl cation (16c) to the β- and 1′-methyl isomers (17c) and (18c) respectively is shown in the Scheme. Ferrocene is depicted as the initiator although any alkylferrocene would serve the same function. (The occurrence of the rearrangements originally discovered was due to the presence of trace amounts of an alkylferrocene contaminant in the alcohol samples used.) Each reversible reaction indicated is merely a variant of the basic reaction given in equation (1), modified by the presence of a substituent in the ferrocene rings. Under thermodynamic control, the equilibrium mixture produced in each case reflects the relative thermodynamic stabilities of the participating carbonium ions [*e.g.* (16c)—(18c)]. Since the α-substituted tertiary cations are appreciably less stable than their β- or 1′-substituted isomers,[1] their concentration at equilibrium is below the level of detection by ^1H n.m.r. spectroscopy. Similarly, the relative equilibrium concentrations of the diferrocenylalkane intermediates [*e.g.* (25a—c)] are too low for detection (*vide supra*) while the amount of the (Me_2C^+) transport agent [*e.g.* (23)] produced is determined by the amount of ferrocene (or alkylferrocene) originally present as initiator. At low concentrations of initiator, all that is observed spectroscopically is a gradual rearrangement of the α-substituted cation to a mixture of the β- and 1′-substituted isomers. The conversion of the α,1′-substituted cations (2) into their β,1′-substituted isomers (3) can be explained by a similar equilibrium controlled rearrangement proceeding *via* diferrocenylalkane intermediates of the types (25d and e).

Evidence supporting the proposed mechanism has been obtained from various experiments. Thus, for any given rearrangement, the rate at which equilibrium between the participating cations is attained is proportional to the concentration of the initiator present. All the α-substituted cations (2a—g), (8c), (11c), (12c), (14), (16c), and (19c) are stable in CF_3CO_2H but rearrange upon addition of ferrocene or an alkylferrocene to the solution. For example, the α-substituted cations (11c) and (12c) of the 1,3-dimethyl series each rearrange in

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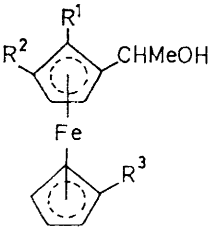
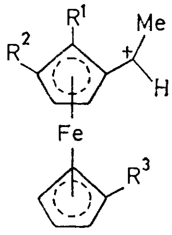
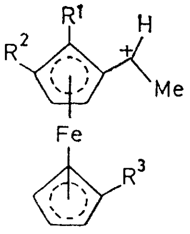
the presence of 1,3-dimethylferrocene to give the isomeric cation (13c). Similarly, each of the cations of the series (8c)—(10c) rearranges in the presence of 1,2-dimethylferrocene to give the same equilibrium mixture of the β- and 1′-substituted isomers (9c) and (10c) respectively in the ratio 3 : 2. Again, addition of methylferrocene to solutions containing either the β-methyl cation (17c) or the 1′-methyl cation (18c) leads to the formation of the same equilibrium mixture of the two cations in which the former predominates (*ca.* 60%). The preponderance of the β-substituted cations in these equilibrium mixtures reflects the greater stabilisation of the ferrocenylalkylium cation system by a β-alkyl substituent than that provided by a 1′-alkyl substituent.[1] Other examples of inter-cation exchange of the (Me_2C^+) group between different series have been found. For example, equimolar amounts of t-butylferrocene and the parent cation (23) react in CF_3CO_2H to give a mixture of the cations (20c), (21c), and (23). Similarly, the cation (23) reacts with 1,1′-di-t-butylferrocene to give a mixture of (3d) and (23), the former predominating at equilibrium.



(26)



(27)



(28)

a; $R^1 = R^3 = Me$; $R^2 = H$
b; $R^2 = R^3 = Me$; $R^1 = H$
c; $R^1 = Me$; $R^2 = R^3 = H$
d; $R^2 = Me$; $R^1 = R^3 = H$
e; $R^3 = Me$; $R^1 = R^2 = H$

Secondary ferrocenylalkylium ions also equilibrate in CF_3CO_2H in the presence of an alkylferrocene initiator. The alcohol precursors (26a—e) were obtained by lithium aluminium hydride reduction of the corresponding acetyl derivatives of methylferrocene[7] and 1,1′-dimethylferrocene.[6] Spectroscopic study of the course of these reactions is complicated by the occurrence of rotational equilibration of the stereoisomeric forms of the cations [(27) $\rightleftharpoons$ (28); see Part IV[3]], which proceeds independently of inter-cation exchange. However, it was established (^1H n.m.r.; see Table 2) that, in CF_3CO_2H containing 1,1′-dimethylferrocene, each of the isomeric cations (27a), (28a), and [(27b/28b) non-separable stereoisomers] gives the same equilibrium mixture containing approximately equal proportions of the *anti*-α-methyl cation (28a) and the β-methyl isomers (27b/28b). The presence of the sterically destabilised *syn*-α-methyl cation (27a) in this mixture was not detected. Similarly, the cations of the methyl series (27c—e) and (28c—e) equilibrate in the presence of methylferrocene to give, in each case, an isomeric mixture containing the cations (28c), (27d/28d), and (27e) ≡ (28e). Again, the presence of the *syn*-α-methyl cation (27c) in the equilibrium mixture was not apparent.

We were unable to effect inter-cation exchange reactions involving ferrocenylalkylium ions of the type ($Fc\overset{+}{C}RPh$; R = H, Me, *etc.*). The failure of these cations to react with ferrocene or alkylferrocenes may be attributed to the presence of the phenyl group which serves to increase the steric bulk and to reduce the electrophilicity of the species. The diferrocenylmethylium cation ($Fc_2\overset{+}{C}H$) proved similarly inert. We were also unable to effect exchange of the (Me_2C^+) group between the cation (23) and ruthenocene, or between the 1-ruthenocenyl-1-methylethylium cation (π-C_5H_5-$RuC_5H_4\overset{+}{C}Me_2$) and ferrocene. Similarly, investigation of the ^1H n.m.r. spectra of CF_3CO_2D solutions containing the last cation and ruthenocene showed that migration of the (Me_2C^+) group between ruthenocene residues does not occur (H–D exchange of the ruthenocene protons only), in contrast to the behaviour of the ferrocenyl system [equation (1)]. These findings are not surprising since it is known that ruthenocene is less reactive than ferrocene towards electrophilic substitution[14] and that ruthenocenylalkylium ions are thermodynamically much more stable (therefore less electrophilic) than their ferrocenyl counterparts.[1]

EXPERIMENTAL

For general details, see Part IV.[3]

1,2-*Dimethylferrocene*.—A solution of 1,2-bishydroxymethylferrocene[15] (2·5 g, 0·01 mol) in ether (50 ml) was added to a stirred mixture of $LiAlH_4$ (1·2 g, 0·03 mol) and $AlCl_3$ (8·0 g, 0·06 mol) in ether (200 ml). After 1 h, excess of hydride was destroyed (EtOAc) and the mixture was poured into water. The ether layer was separated, washed (H_2O), dried (Na_2SO_4), and evaporated. The residue was dissolved in light petroleum and chromatographed. Light petroleum eluted 1,2-dimethylferrocene (2·0 g, 93%), a yellow solid, m.p. 33—34° (lit.,[16] 34—36°).

1,3-*Dimethylferrocene*.—A solution of 3-formylmethylferrocene[17] (2·8 g, 0·01 mol) in ether (50 ml) was treated with $LiAlH_4$ (1·2 g, 0·03 mol) and $AlCl_3$ (8·0 g, 0·06 mol) in ether (200 ml) as described in the preceding experiment. A similar work-up gave 1,3-dimethylferrocene (2·0 g, 92%) as a yellow liquid (lit.,[16] liquid).

Preparation of Ketones.—The acetylations of methylferrocene, t-butylferrocene, 1,1′-dimethylferrocene, 1,1′-diethylferrocene, 1,1′-di-isopropylferrocene, and the 1,1′-(polymethylene)ferrocenes [$(CH_2)_{3-5}$] have been reported previously (see refs. 18 and 19).

Acetylation of 1,1′-*Di-t-butylferrocene*.—BF_3,Et_2O (40 ml) was added dropwise to a stirred solution of Ac_2O (20 ml) and 1,1′-di-t-butylferrocene (23 g, 0·08 mol) in CH_2Cl_2 (200 ml) at 0°. The solution was stirred for 2 h at 0°

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and then at room temperature overnight, washed in turn with water containing $TiCl_3,H_2O$, and aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated. The residue was dissolved in light petroleum and chromatographed. Light petroleum eluted unchanged starting material. Light petroleum–ether (49 : 1) eluted 2-*acetyl*-1,1′-*di*-*t*-*butylferrocene* (1·1 g, 3%), a dark red liquid (Found: C, 70·4; H, 8·2. $C_{20}H_{28}FeO$ requires C, 70·6; H, 8·3%), τ 5·35 (1H, t, 3-H), 5·5—5·7 (2H, m, 4- and 5-H), 5·75—5·95 (4H, m, C_5H_4), 7·59 (3H, s, Ac), and 8·64 and 8·78 (9H and 9H, 2 × s, Bu^t). Light petroleum-ether (9 : 1) eluted 3-*acetyl*-1,1′-*di*-*t*-*butylferrocene* (12·8 g, 29%), a dark red liquid (Found: C, 70·3; H, 8·2%), τ 5·15—5·35 (2H, m, 2- and 4-H), 5·5—5·65 (1H, m, 5-H), 5·85—6·1 (4H, m, C_5H_4), 7·64 (3H, s, Ac), and 8·77 and 8·80 (9H and 9H, 2 × s, Bu^t).

Acetylation of 1,2-*Dimethylferrocene*.—This reaction was carried out by the method described above. The product was chromatographed in light petroleum which eluted unchanged alkylferrocene (8% recovery). Light petroleum–ether (9 : 1) eluted the 2,3-*dimethyl-ketone* (8a) (29%), an orange-red liquid (Found: C, 65·8; H, 6·2. $C_{14}H_{16}FeO$ requires C, 65·7; H, 6·3%), τ 5·55 and 5·74 (1H and 1H, 2 × d, C_5H_2), 6·02 (5H, s, π-C_5H_5), 7·67 (3H, s, Ac), and 7·76 and 8·04 (3H and 3H, 2 × s, Me). The same solvent eluted the 1′,2′-*dimethyl-ketone* (10a) (40%), an orange-red liquid (Found: C, 65·7; H, 6·2%), τ 5·52 and 5·77 (2H and 2H, 2 × t, C_5H_4), 6·02 (3H, m, C_5H_3), 7·68 (3H, s, Ac), and 8·17 (6H, s, Me). The same solvent eluted the 3,4-*dimethyl-ketone* (9a) (20%), an orange solid, m.p. 90—92° (Found: C, 65·8; H, 6·2%), τ 5·37 (2H, s, C_5H_2), 5·99 (5H, s, π-C_5H_5), 7·67 (3H, s, Ac), and 8·02 (6H, s, Me).

Acetylation of 1,3-*Dimethylferrocene*.—This reaction was carried out as described above. Chromatography of the product in light petroleum–ether (9 : 1) gave in order of elution: the 2,5-*dimethyl-ketone* (11a) (7%), an orange-red liquid (Found: C, 65·6; H, 6·25%), τ 5·80 (2H, s, C_5H_2), 5·97 (5H, s, π-C_5H_5), 7·50 (3H, s, Ac), and 7·80 (6H, s, Me); the 2,4-*dimethyl-ketone* (12a) (25%), an orange-red liquid (Found: C, 65·8; H, 6·3%), τ 5·52 and 5·64 (1H and 1H, 2 × d, C_5H_2), 5·88 (5H, s, π-C_5H_5), 7·66 (3H, s, Ac), and 7·78 and 8·06 (3H and 3H, 2 × s, Me); the 1′,3′-*dimethyl-ketone* (13a) (44%), an orange solid, m.p. 48—49° (Found: C, 65·8; H, 6·3%), τ 5·40 and 5·65 (2H and 2H, 2 × t, C_5H_4), 6·06 (3H, m, C_5H_3), 7·68 (3H, s, Ac), and 8·18 (6H, s, Me).

Trideuterioacetylation of 1,1′-*Dimethylferrocene*.—Acylation of 1,1′-dimethylferrocene using CD_3COCl–$AlCl_3$ was carried out as for the corresponding acetylation reaction.[6] The ^1H n.m.r. spectra of the α- and β-acyl derivatives were identical with those of their protio-analogues except for the absence of acetyl singlets.

Preparation of Tertiary Alcohols.—The alcohols (1), (4), (8b)—(13b), and (16b)—(21b) were prepared by the addition of methyl-lithium to the corresponding ketones. One such experiment is described below. Analytical data, *etc*., for these compounds are in Table 3.

2-(3-*Methylferrocenyl*)*propanol*-2-*ol* (17b). A solution of the ketone (17a) (0·24 g, 0·001 mol) in ether (20 ml) was added dropwise to an excess of MeLi in ether (30 ml) and the solution was stirred for 1 h. The excess of MeLi was destroyed (MeOH) and the solution was poured into water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in light petroleum–ether (3 : 1) and chromatographed. This solvent eluted a single yellow band which afforded the *alcohol* (17b), a yellow solid, m.p. 35—36°, τ 5·87 (5H, s, π-C_5H_5), 5·92 (3H, m, C_5H_3), 7·92 (1H, s, OH), and 8·04 and 8·55 (3H and 6H respectively, 2 × s, Me).

2-*Ruthenocenylpropan*-2-*ol*.—This alcohol was prepared by the addition of methyl-lithium to acetylruthenocene[20] as described above. The compound was obtained as a pale yellow solid, m.p. 80—82° (Found: C, 54·2; H, 5·7. $C_{13}H_{16}ORu$ requires C, 53·9; H, 5·6%), τ 5·33 (5H, s, π-C_5H_5), 5·2—5·5 (4H, m, C_5H_4), 8·53 (6H, s, Me), and 8·22 (1H, s, OH).

TABLE 3

Alcohols

Compound	M.p. (°C) [a]	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
(1a)		$C_{15}H_{20}FeO$	66·1	7·4	66·2	7·4
(1b)		$C_{17}H_{24}FeO$	68·1	8·1	68·0	8·1
(1c)		$C_{19}H_{28}FeO$	69·4	8·6	69·5	8·6
(1d)		$C_{21}H_{32}FeO$	70·9	9·0	70·8	9·1
(1e)	74—76	$C_{16}H_{20}FeO$	67·6	7·2	67·6	7·1
(1f)	70—71	$C_{17}H_{22}FeO$	68·4	7·4	68·5	7·4
(1g)	89—91	$C_{18}H_{24}FeO$	69·1	7·7	69·2	7·8
(4a) [b]		$C_{15}H_{20}FeO$				
(4b)		$C_{17}H_{24}FeO$	68·1	8·0	68·0	8·1
(4c)		$C_{19}H_{28}FeO$	69·1	8·5	69·5	8·6
(4d)		$C_{21}H_{32}FeO$	71·1	8·9	70·8	9·1
(4e) [b]		$C_{16}H_{20}FeO$				
(4f)		$C_{17}H_{22}FeO$	68·5	7·4	68·5	7·4
(4g)	57—59	$C_{18}H_{24}FeO$	69·1	7·8	69·2	7·8
(8b)		$C_{15}H_{20}FeO$	66·1	7·3	66·2	7·4
(9b)	58—60	$C_{15}H_{20}FeO$	66·1	7·4	66·2	7·4
(10b)		$C_{15}H_{20}FeO$	66·2	7·3	66·2	7·4
(11b)		$C_{15}H_{20}FeO$	66·0	7·4	66·2	7·4
(12b)		$C_{15}H_{20}FeO$	66·3	7·3	66·2	7·4
(13b)		$C_{15}H_{20}FeO$	66·2	7·4	66·2	7·4
(16b)		$C_{14}H_{18}FeO$	65·0	7·0	65·1	7·0
(17b)	35—36	$C_{14}H_{18}FeO$	65·0	7·0	65·1	7·0
(18b)		$C_{14}H_{18}FeO$	65·1	6·9	65·1	7·0
(19b)		$C_{17}H_{24}FeO$	68·1	8·0	68·0	8·1
(20b)		$C_{17}H_{24}FeO$	68·1	8·1	68·0	8·1
(21b)		$C_{17}H_{24}FeO$	68·1	8·0	68·0	8·1

[a] Unless liquid. [b] Ref. 2*b*.

Preparation of 1,1,1-*Trideuterio*-2-(*dimethylferrocenyl*)-*propan*-2-*ols*.—Addition of MeLi to 2- and 3-(trideuterioacetyl)-1,1′-dimethylferrocene according to the method described above gave the corresponding alcohols whose ^1H n.m.r. spectra were identical with those of their protio-analogues except that the (CMe_2) signal intensity was reduced by one half.

Preparation of Secondary Alcohols.—The alcohols (26a and c—e) were prepared and (26a and c) separated into their diastereoisomeric forms by literature methods.[21]

1-(1′,3-*Dimethylferrocenyl*)*ethanol* (26b).—A solution of 3-acetyl-1,1′-dimethylferrocene (2·6 g, 0·01 mol) in ether (20 ml) was added to an excess of $LiAlH_4$ in ether (80 ml) and the mixture was stirred for 1 h. The excess of hydride was destroyed (EtOAc) and the mixture was poured into water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was dissolved in light petroleum–ether (3 : 1) and chromatographed. This solvent eluted the *alcohol* (26b), a yellow liquid (Found: C, 65·3; H, 7·1. $C_{14}H_{18}FeO$ requires C, 65·1; H, 7·0%), τ 5·52 (1H, q, CH), 5·9—6·0 (7H, m, ferrocenyl), 8·00 (1H, s, OH), 8·06 (6H, s, ring Me), and 8·12 (3H, d, Me).

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[21] E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 4216.

2-*Isopropyl*-1,1′-*dimethylferrocene* (7).—A solution of the alcohol (1a) (0·26 g, 0·001 mol) in ether (20 ml) was added to a stirred mixture of $LiAlH_4$ (0·06 g, 0·0015 mol) and $AlCl_3$ (0·4 g; 0·003 mol) in ether (20 ml). After 0·5 h, the excess of hydride was destroyed (EtOAc) and the reaction was worked-up as above. The product was dissolved in light petroleum and chromatographed. Light petroleum eluted a single band which afforded the *alkylferrocene* (7) (0·23 g, 96%), a yellow liquid (Found: C, 70·1; H, 7·8. $C_{15}H_{20}Fe$ requires C, 70·3; H, 7·9%), τ 6·10 (7H, m, ferrocenyl), 7·32 (1H, m, C*H*Me$_2$), 8·07 (6H, s, ring Me), and 8·68 and 9·01 (3H and 3H, 2 × d, CH*Me*$_2$).

3-*Isopropyl*-1,1′-*dimethylferrocene* (6).—This compound was obtained by reduction of the alcohol (4a) exactly as above. The *alkylferrocene* (6) (95%) was obtained as a yellow liquid (Found: C, 70·2; H, 7·9%), τ 5·95—6·2 (7H, m, ferrocenyl), 7·50 (1H, m, C*H*Me$_2$), 8·06 and 8·08 (6H, 2 × s, ring Me), and 8·87 (6H, d, CH*Me*$_2$).

Quenching Experiment.—The alcohol (1a) (0·27 g) was dissolved in CF_3CO_2H (2 ml) containing 1,1′-dimethylferrocene (5 mg). When rearrangement of the cation produced [*i.e.* (2a) ⟶ (3a)] was complete (^1H n.m.r.) after 20 min, the solution was poured into aqueous NaOH (1M; 50 ml) and the resulting solution was extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was dissolved in light petroleum and chromatographed. Light petroleum eluted a trace of 1,1′-dimethylferrocene followed by 2-(1′,3-*dimethylferrocenyl*)*propene* (5) (0·13 g, 51%), an unstable orange oil, for which satisfactory analytical data were not obtained, τ 4·90, 5·13 (1H and 1H, 2 × m, vinyl), 5·7—6·1 (7H, m, ferrocenyl), and 7·98, 8·01, and 8·08 (3H each, 3 × s, Me). This alkene (0·125 g) was dissolved in EtOH (20 ml) and hydrogenated over PtO_2. When uptake of H_2 had ceased, the solution was filtered, diluted with water (100 ml), and extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in light petroleum and chromatographed, affording as the sole product (6) (0·11 g, 92%), identical (^1H n.m.r., i.r., g.l.c. retention time) with the product already described.

Fragmentation of 2,2-*Diferrocenylpropane.*—Compound [8] (22) (100 mg) was dissolved in CF_3CO_2H (2 ml). The ^1H n.m.r. spectrum of the brown solution obtained was identical with that of an equimolar mixture of the cation (23) and ferrocene in CF_3CO_2H (see Table 1).

H–D *Exchange Experiments.*—The ^1H n.m.r. spectra of the cation (23), generated from an ultra-pure sample (preparative t.l.c.) of 2-ferrocenylpropan-2-ol [16] in CF_3CO_2H and in CF_3CO_2D, were identical. No diminution in intensity of the signals in the CF_3CO_2D spectrum was observed over a period of several hours at 33° (*i.e.*, no H–D exchange). Addition of ferrocene to a solution of the cation (23) in CF_3CO_2D gave a spectrum in which the intensities of the ring proton signals steadily decreased relative to the intensity of the (Me_2C^+) signal (*i.e.*, H–D exchange of the ring protons). The ^1H n.m.r. spectrum of the 1-ruthenocenyl-1-methylethylium cation (Table 1), obtained from 2-ruthenocenylpropan-2-ol in CF_3CO_2D, showed no evidence of H–D exchange over several hours at 33°. An equimolar solution of the same cation and ruthenocene in CF_3CO_2D gave a spectrum in which the intensity of the ruthenocene signal only steadily decreased (*i.e.*, H–D exchange) but the intensities of the cation signals remained unchanged (*i.e.*, no H–D exchange).

Monitoring of Rearrangements.—The ^1H n.m.r. spectra of all the cations investigated are readily distinguishable (Tables 1 and 2). Solutions of the α-substituted cations (2a—g), (8c), (11c), (12c), (14), (16c), and (19c), generated from ultra-pure samples (preparative t.l.c.) of the corresponding alcohols in CF_3CO_2H, gave spectra which were unchanged over several hours at 33° or higher temperatures. Addition of small amounts of ferrocene or an alkylferrocene to these solutions caused the signals of the original cation to diminish steadily and be replaced by new signals characteristic of β-substituted and/or 1′-substituted isomers. The rates of spectral change were observed to increase with increasing concentration of initiator added. In the rearrangement of the deuterium labelled cation [(14) ⟶ (15)], the spectrum of the product showed that the CD_3 group was retained exclusively at C_{exo}.

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