

## Stable Carbocations. Part 15.<sup>1</sup> Double-shift Rearrangements of Ferrocenylcarbenium Ions

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In solution in trifluoroacetic acid, ferrocenylcarbenium ions of the type  $\text{Fc}\overset{\oplus}{\text{C}}\text{R}^1\text{CR}^2\text{R}^3\text{R}^4$  undergo equilibrative rearrangement by interchange of  $\text{R}^1$  with  $\text{R}^2$ ,  $\text{R}^3$ , or  $\text{R}^4$ . For secondary carbenium ions ( $\text{R}^1 = \text{H}$ ), the position of equilibrium lies far towards the rearranged species, whereas tertiary ions ( $\text{R}^1 = \text{Me}$  or  $\text{Ph}$ ) give equilibrium mixtures containing substantial amounts of the precursor and its rearrangement product. Introduction of a  $\text{t}$ -butyl substituent into the ferrocenyl group of  $\text{Fc}\overset{\oplus}{\text{C}}\text{MePr}^i$  destabilises the ion, which is converted into its  $\overset{\oplus}{\text{C}}\text{HBU}^t$  isomer.

Cations of the type  $\text{Fc}\overset{\oplus}{\text{C}}\text{R}^1\text{CH}_2\text{R}^2$  do not rearrange. The mechanism of the reaction has been investigated by kinetic methods and by study of the properties of sterically constrained species. Evidence has been obtained suggesting that rearrangement is assisted by neighbouring-group participation by ferrocenyl. Alcohols of the type  $\text{FcCR}_2\text{CR}'_2\text{OH}$  undergo acid-promoted heterolysis and rearrangement to  $\text{FcCRR}'_2$ .

ONE of the most commonly encountered rearrangements of carbenium ions involves 1,2-shift of a group to the electron-deficient carbon atom.<sup>2</sup> In most reactions of this type, the initial and rearranged carbocations intervene as transient intermediates and direct study of the rearrangement step requires the use of stabilising 'super-acid' solvents, usually at low temperatures.<sup>3</sup> In the course of investigations of the properties of ferrocenylcarbenium ions, which are stable in acidic media, we discovered<sup>4</sup> that cations of the type  $\text{Fc}\overset{\oplus}{\text{C}}\text{HCR}_3$  rearrange in solution in trifluoroacetic acid to give isomers  $\text{Fc}\overset{\oplus}{\text{C}}\text{RCHR}_2$  resulting from a double-shift rearrangement. Since the behaviour of such cations can be monitored conveniently by <sup>1</sup>H n.m.r. spectroscopy, we have studied the scope and mechanism of this reaction and we now report the results.

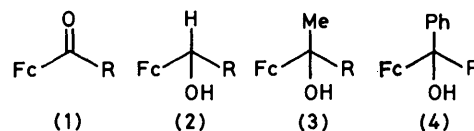
**Synthetic Methods.**—A series of acylferrocenes (1a—k), prepared from ferrocene by Friedel–Crafts reactions, was converted into the alcohols (2a—j), (3a—f), and (4e and k) by treatment with lithium aluminium hydride, methyl-lithium, and phenyl-lithium, respectively. Reactions of the more highly substituted ketones with these lithio-reagents proceeded sluggishly and we were unable to prepare the alcohols (3g) and (4d) from the ketones (1g) and (1d), respectively. In the former case,

<sup>1</sup> Part 14, T. S. Abram and W. E. Watts, *J.C.S. Perkin I*, preceding paper.

<sup>2</sup> For review articles, see C. J. Collins, *Quart. Rev.*, 1960, **14**, 357; J. L. Fry and G. J. Karabatsos in 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1970, vol. II, ch. 14; D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, 1972, **9**, 179; T. S. Stevens and W. E. Watts, 'Selected Molecular Rearrangements,' van Nostrand-Reinhold, London, 1973, ch. 2; T. H. Lowry and K. S. Richardson, 'Mechanism and Theory in Organic Chemistry,' Harper and Row, New York, 1976, ch. 6.

a small yield of  $\text{FcCMe}_2\text{OH}$  was isolated, resulting from elimination of trityl-lithium from the intermediate complex  $[\text{FcC}(\text{OLi})(\text{Me})\text{CPh}_3]$  and addition of methyl-lithium to the acetylferrocene liberated.

The 2-ferrocenylalkanols (5b) and (5c) were obtained by treatment of the ester (5a) with methylmagnesium



- |                                 |                        |
|---------------------------------|------------------------|
| a; R = $\text{CH}_2\text{Bu}^t$ | g; R = $\text{CPh}_3$  |
| b; R = $\text{CH}_2\text{Ph}$   | h; R = cyclopropyl     |
| c; R = $\text{Pr}^i$            | i; R = cyclobutyl      |
| d; R = $\text{CHPh}_2$          | j; R = cyclopentyl     |
| e; R = $\text{Bu}^t$            | k; R = $\text{CHMePh}$ |
| f; R = $\text{CMePh}_2$         |                        |

Fc = ferrocenyl (throughout)

iodide and phenylmagnesium bromide, respectively. The alcohol (6d) was similarly obtained from the ester (6c), which was prepared from the cyanide (6a) by hydrolysis and esterification of the resulting acid (6b). The ( $\text{t}$ -butylferrocenyl)alkanols (7a—c) and (8a—d) were available from earlier studies.<sup>5,6</sup>

**Carbocation Rearrangements.**—Ferrocenylcarbenium

<sup>3</sup> See G. A. Olah and J. A. Olah in 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1970, vol. II, ch. 17; G. A. Olah, *Angew. Chem. Internat. Edn.*, 1973, **12**, 173.

<sup>4</sup> Preliminary communication, T. D. Turbitt and W. E. Watts, *J. Organometallic Chem.*, 1973, **57**, C78.

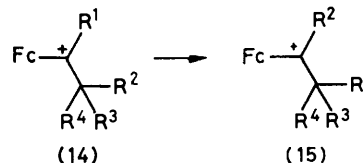
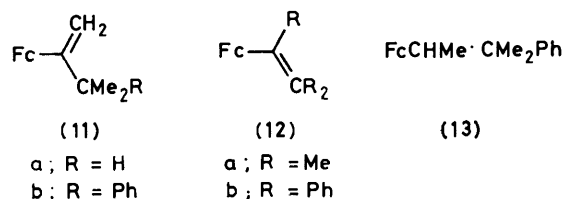
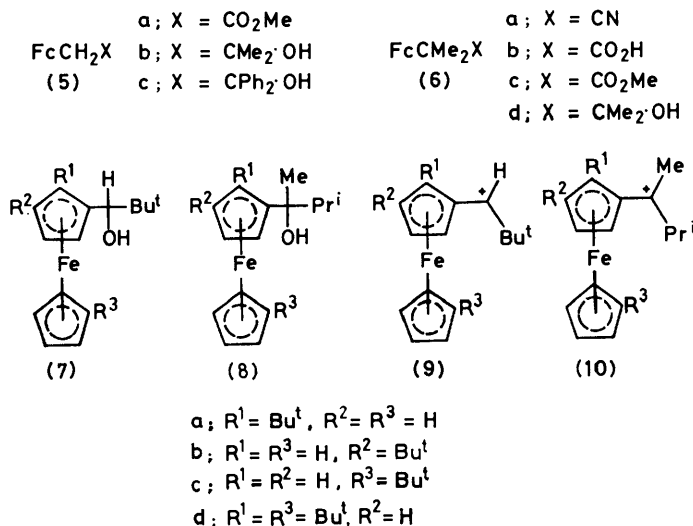
<sup>5</sup> T. S. Abram and W. E. Watts, *J. Organometallic Chem.*, 1975, **86**, 109.

<sup>6</sup> T. S. Abram and W. E. Watts, *J.C.S. Perkin I*, 1975, 116.

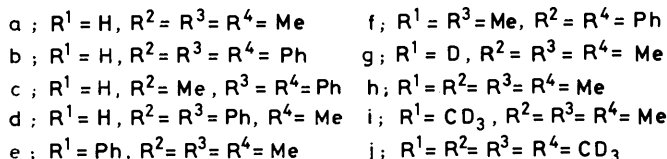
ions are formed instantaneously from 1-ferrocenyl-alkanols and -alkenes in trifluoroacetic acid and give characteristic, readily interpretable  $^1\text{H}$  n.m.r. spectra in this solvent. The cations resulting from acid-promoted heterolysis of the alcohols (2a—d and h—j), (3a—d), and (4k) were stable; no changes were detected in their

(15b) was established both from its characteristic spectrum and from its conversion into the alkene (12b) on quenching.

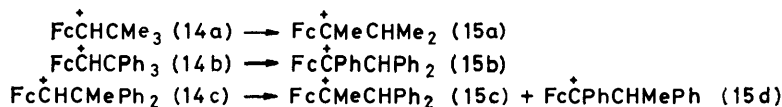
The deuterio-analogue (14g) of the cation (14a) also rearranged, to give a product (15g) in which the deuterium label was completely retained. The isomeric tertiary carbenium ions (14e) and (15e), obtained by dissolution of the alcohol (4e) and the alkene (11b) respectively in trifluoroacetic acid, each rearranged to give an equilibrium mixture of (14e) and (15e) in which the latter predominated (69% at 328 K). Similarly, the cation (14f) obtained from the alcohol (3f) gave finally a mixture of (14f) and its isomer (15f) (77% at 328 K).



spectra during extended periods. Under these conditions, apparently (see later), secondary and tertiary ferrocenylcarbenium ions containing a  $\text{CH}_2\text{R}$  ( $\text{R} = \text{Bu}^t$  or  $\text{Ph}$ ) or  $\text{CHR}_2$  group ( $\text{R}_2 = \text{Me}_2$ ,  $\text{Ph}_2$ ,  $[\text{CH}_2]_n$ , or  $\text{MePh}$ ) attached to the formal  $\text{C}^+$  atom do not rearrange. When solutions of these cations were quenched (aq.  $\text{NaHCO}_3$ ), mixtures of addition and deprotonation products were formed and these were separated and characterised in a few cases. For example,  $\text{Fc}\dot{\text{C}}\text{MePr}^i$  gave a mixture of the alkenes (11a) and (12a) together with the starting alcohol (3c), and  $\text{Fc}\dot{\text{C}}\text{MeCMe}_2\text{Ph}$  (see later) gave mainly the alkene (11b). Hydrogenation of compound (11b) gave the alkylferrocene (13).

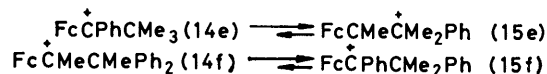


The occurrence of a degenerate (methyl-scrambling) rearrangement of the cation (14h) was indicated by the behaviour of the deuterium-labelled analogue (14i) which, in solution in trifluoroacetic  $[\text{D}_2\text{H}]$ acid, was slowly converted into the fully deuteriated species (14j). We have previously shown<sup>8</sup> that, with ferrocenylalkylium



In contrast, the ferrocenylcarbenium ions formed from the alcohols (2e—g), (3f), and (4e) were unstable in solution in trifluoroacetic acid, undergoing rearrangements which could be monitored by  $^1\text{H}$  n.m.r. spectroscopy. The secondary carbenium ions (14a and b) were cleanly converted into a single tertiary isomer in each case. The cation (14c) [ $\equiv$  (14d)], on the other hand, gave a mixture of tertiary isomers (15c and d) in which the product of methyl migration predominated. The products (15a), (15c), and (15d)<sup>7</sup> were identified by comparison of their spectra with those of the cations generated unambiguously from the alcohols (3c), (3d), and (4k), respectively. The structure of the product

ions, only those protons attached to the carbon atoms directly bonded to the formal  $\text{C}^+$  atom undergo H-D exchange in trifluoroacetic  $[\text{D}_2\text{H}]$ acid. Incorporation of



deuterium by the t-butyl group of (14i) can occur only if the associated methyl groups can exchange with the group already attached to the  $\text{C}^+$  atom.

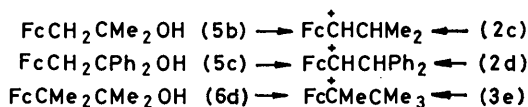
We have already reported<sup>6</sup> the rearrangement of the (2-t-butylferrocenyl)carbenium ion (10a) to its isomer

<sup>8</sup> W. Crawford and W. E. Watts, *J. Organometallic Chem.*, 1976, **110**, 257.

<sup>7</sup> T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

(9a); a similar reaction was found for the 1',2-di-*t*-butyl analogue (10d), which afforded (9d). When solutions of the cation (9d) were quenched (aq. NaHCO<sub>3</sub>), the alcohol (7d) was the exclusive product. The secondary 3- and 1'-*t*-butyl-substituted cations (9b and c) underwent rearrangement in the reverse sense, giving their tertiary isomers (10b) and (10c), respectively.

Heterolysis of the 2-ferrocenylalkanols (5b), (5c), and (6d) in solution in trifluoroacetic acid was accompanied by instantaneous rearrangement to give cleanly the



corresponding 1-ferrocenylalkyl cations, which were identified by comparison of their <sup>1</sup>H n.m.r. spectra with those of authentic specimens generated from the alcohols (2c), (2d), and (3e). In these reactions,\* it appears possible that elimination of water from the protonated alcohol precursors proceeds synchronously with 1,2-shift, giving the products directly.

**Kinetics and Mechanism.**—The rates of rearrangement of the cations (9b and c), (10a and d), and (14a and g) in solution in trifluoroacetic acid at 328 K were measured by using <sup>1</sup>H n.m.r. spectroscopy (Experimental section); the first-order rate constants are in Table I. The rate of

TABLE I  
Rate and equilibrium constants

Rearrangement	T/K	Rate constant 10 <sup>5</sup> k/s <sup>-1</sup>	<i>k</i> <sub>ret</sub>	<i>K</i> <sub>eq</sub>		
(14a) → (15a)	313	1.20 ± 0.008	1.00	> 20		
	323	4.38 ± 0.001				
	328	8.19 ± 0.005				
	333	15.00 ± 0.002				
	343	41.70 ± 0.033				
(14b) → (15b)	328	> 5 × 10 <sup>8</sup>	> 600	> 20		
	(14e) → (15e)	323			2.68 ± 0.002	2.45
		328			4.29 ± 0.009	2.23
		333			9.31 ± 0.022	2.03
		338			15.20 ± 0.012	1.86
343	24.54 ± 0.024	1.70				
(14f) → (15f)	328	63.80 ± 0.10	7.79	3.35		
(14g) → (15g)	328	8.00 ± 0.011	0.98	> 20		
(15e) → (14e)	323	1.10 ± 0.002	0.24	0.41		
	328	1.99 ± 0.002			0.45	
	333	4.58 ± 0.011			0.49	
	338	8.18 ± 0.007			0.54	
	343	14.40 ± 0.014			0.59	
(15f) → (14f)	328	19.1 ± 0.05	2.33	0.30		
(9b) → (10b)	328	3.34 ± 0.009	0.41	> 20		
(9c) → (10c)	328	5.35 ± 0.011	0.65	> 20		
(10a) → (9a)	328	17.12 ± 0.037	2.09	> 20		
(10d) → (9d)	328	18.5 ± 0.05	2.26	> 20		

rearrangement of the cation (14b) was too fast to be measured by this method and only a lower limit for the rate constant could be estimated. The forward and reverse rate constants for the reactions (14e) ⇌ (15e) and (14f) ⇌ (15f) were also obtained from the observed rate and equilibrium constants [*k*<sub>obs</sub> = *k*<sub>f</sub> + *k*<sub>r</sub> = *k*<sub>f</sub>(1 + *K*<sub>eq</sub>)/*K*<sub>eq</sub>]. For the former reaction, good agree-

\* A report of the independent discovery of these rearrangements was published (C. C. Lee, S. C. Chen, W. J. Pannekoek, and R. G. Sutherland, *J. Organometallic Chem.*, 1976, **118**, C17) following the completion of this work.

ment was found between rate constants calculated from kinetic runs in which equilibrium was approached from either direction. Additionally, the rates of the reactions (14a) → (15a) and (14e) ⇌ (15e) were measured at several temperatures in the range 313–343 K; the derived thermodynamic quantities are in Table 2.

If we consider these double-shift rearrangements as reversible processes, the position of equilibrium in each case is determined by the relative thermodynamic

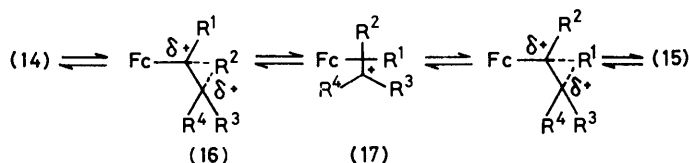
TABLE 2

Thermodynamic quantities<sup>a</sup>

Rearrangement	<i>E</i> <sub>a</sub> kJ mol <sup>-1</sup>	Δ <i>H</i> <sup>‡</sup> kJ mol <sup>-1</sup>	<i>T</i> Δ <i>S</i> <sup>‡</sup> kJ mol <sup>-1</sup>
(14a) → (15a)	106.2	103.7	-2.4
(14e) → (15e)	105.0	102.5	-4.8
(15e) → (14e)	121.0	118.5	+7.8

<sup>a</sup> At 298 K.

stabilities of the participating cations. As expected,<sup>9</sup> the disparity in stability between the secondary carbenium ions (9b and c) and (14a–c) and their tertiary isomers (10b and c) and (15a–d) leads to equilibrium mixtures in which the latter largely predominate (>95%; *i.e.* *k*<sub>f</sub>/*k*<sub>r</sub> > 20; Δ*G*<sup>o</sup> > 8.2 kJ mol<sup>-1</sup> at 328 K). In the case of the tertiary (2-*t*-butylferrocenyl)carbenium ions (10a and d), however, steric repulsion between the proximate Bu<sup>t</sup> and CMePr<sup>i</sup> groups raises the energies of the conformations in which *p*<sub>π</sub>-*p*(*d*)<sub>π</sub> conjugative stabilisation of the FcC<sup>+</sup> system is maximised, such that these ions are thermodynamically less stable than their secondary isomers (9a and d) for which this strain is relieved and which predominate (>95%) in the equilibrium mixtures. For the two FcCMeR ⇌ FcCPhR equilibria studied, the position of equilibrium favours the CPh species in the (14f) ⇌ (15f) reaction, but the CMe species in the (14e) ⇌ (15e) mixture. In the latter case, however, a statistical factor favours the forward reaction (one of three Me groups may migrate) over the reverse (only one Ph group may migrate) whereas, for the former equilibrium, forward and reverse reactions are equally favoured statistically.

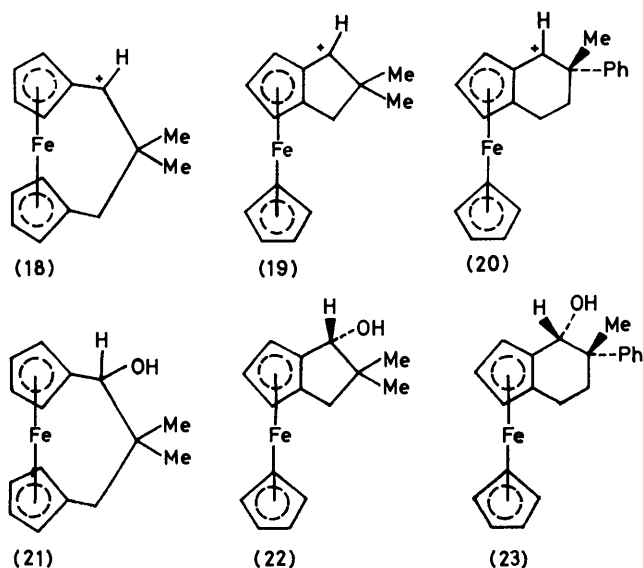


SCHEME 1

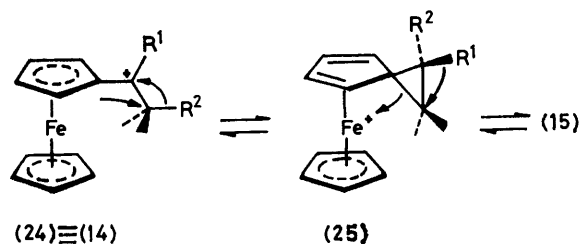
The mechanism of these rearrangements must involve sequential 1,2-shifts with the first migration [*e.g.* (14) → (17); Scheme 1] rate-determining. The variation in the relative rates of rearrangement for the series (Table I) is in accord with a transition state [*cf.* (16)] in which there is appreciable development of positive charge at the migration origin (C<sub>β</sub>). Thus,

<sup>9</sup> T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 185.

rearrangement is disfavoured for cations containing a  $\overset{+}{C}CH_2R$  group but facilitated in the presence of electron-donating  $C_\beta$ -substituents, with the effect of  $Ph > Me$ . Consistently, the rearrangement of (14f) is faster (*ca.* 32 times) than that of (15e); these reactions each involve migration of Ph from  $C_\beta$  to an  $Fc\overset{+}{C}Me$  terminus but differ in the substitution at the migration origin,  $CMePh$  for (14f) and  $CMe_2$  for (15e). The faster rearrangement



(*ca.* 4.5 times) of (15f) than of (14e), and the ready rearrangement of (14b), can be similarly rationalised. In the last example, as in some other reactions, relief of steric crowding at the migration origin may also encourage rearrangement. Substitution of the ferrocenyl group of (14a) by a 3- or 1'-*t*-butyl group [*i.e.* (9b) and



SCHEME 2

(9c) respectively] causes a reduction in the rate of rearrangement since, in these systems, increased electron donation from the ferrocenyl group acts to reduce the electrophilicity of  $C_\alpha$ .

The mechanism shown in Scheme 1, however, does not account for the properties of the bridged secondary carbenium ions (18)—(20) generated from the corresponding secondary alcohols (21)—(23). Under conditions

\* However, the sterically crowded 1-*t*-butyl[3]ferrocenophan-1-yl cation does undergo double-shift rearrangement (see A. D. de Groot, C. de Haan, H. B. Hanekamp, A. C. Joha, and E. W. B. de Leer, *J. Organometallic Chem.*, 1976, **122**, 241).

<sup>10</sup> T. S. Abram and W. E. Watts, *J.C.S. Perkin I*, 1975, 113.

where unbridged analogues [*e.g.* (14a), (14c), and (15e)] isomerise readily, these cations resist double-shift rearrangement to more stable tertiary carbenium ions. We earlier obtained indirect evidence<sup>6</sup> to suggest that rearrangement of a cation of the type (24) may proceed with neighbouring-group participation by ferrocenyl and reversible formation of a short-lived spiro-diene intermediate (25) (Scheme 2). The steric constraints imposed upon the bridging groups of the cations (18)—(20), however, would prohibit formation of such spiro-cyclic cations. If anchimeric assistance by ferrocenyl and formation of a spiro-diene intermediate are prerequisites for double-shift rearrangement, then the failure of these bridged cations to rearrange can be rationalised.\* However, if species of the type (25) do intervene in the earlier reactions, then they are unstable with respect to cyclopropyl ring-opening and rearrangement to ferrocenylcarbenium ions, and their lifetimes in solution in trifluoroacetic acid are too short to permit <sup>1</sup>H n.m.r. spectroscopic detection.

## EXPERIMENTAL

For general details, see Part 4.<sup>7</sup> Analytical data, *etc.*, for the new compounds prepared are in Table 3.

*Preparation of Ketones.*—The ketones (1a—k) were

TABLE 3  
New compounds

Compound	M.p. (°C)	Formula	Found		Required	
			C (%)	H (%)	C (%)	H (%)
(1d)	188—189	C <sub>24</sub> H <sub>20</sub> FeO	75.8	5.4	75.8	5.3
(1f)	149—151	C <sub>25</sub> H <sub>22</sub> FeO	76.0	5.7	76.2	5.6
(1g)	211—212	C <sub>30</sub> H <sub>24</sub> FeO	78.7	5.4	79.0	5.3
(2d)	134—135	C <sub>24</sub> H <sub>22</sub> FeO	75.2	6.2	75.4	5.8
(2f)	164—166	C <sub>25</sub> H <sub>24</sub> FeO	75.7	5.9	75.8	6.1
(2g)	168—171	C <sub>30</sub> H <sub>26</sub> FeO	79.0	5.9	78.6	5.7
(3d)	134—136	C <sub>25</sub> H <sub>24</sub> FeO	75.9	6.4	75.8	6.1
(3f)	120—122	C <sub>26</sub> H <sub>26</sub> FeO	<i>a</i>	<i>a</i>		
(4e)	83—85	C <sub>21</sub> H <sub>24</sub> FeO	72.3	7.1	72.4	7.0
(5b)	51—52	C <sub>14</sub> H <sub>18</sub> FeO	65.2	7.1	65.1	7.0
(5c)	72—73	C <sub>24</sub> H <sub>22</sub> FeO	75.2	6.0	75.4	5.8
(6d)	65—67	C <sub>18</sub> H <sub>22</sub> FeO	66.7	7.8	67.2	7.8
(7d)	73—74	C <sub>26</sub> H <sub>26</sub> FeO	72.1	9.3	71.9	9.4
(11a)	(Liquid)	C <sub>15</sub> H <sub>16</sub> Fe	70.9	7.0	70.9	7.1
(11b)	89—90	C <sub>21</sub> H <sub>22</sub> Fe	75.8	6.6	76.4	6.7
(12b)	178—180	C <sub>30</sub> H <sub>24</sub> Fe	81.4	5.4	81.8	5.5
(13)	(Liquid)	C <sub>21</sub> H <sub>24</sub> Fe	75.9	7.4	75.9	7.3
(21)	110—112	C <sub>15</sub> H <sub>18</sub> FeO	66.6	6.7	66.7	6.7
(23)	85—86	C <sub>21</sub> H <sub>22</sub> FeO	73.1	6.4	72.8	6.4

<sup>a</sup> Decomposes; satisfactory analytical results were not obtained.

prepared by standard Friedel-Crafts reactions between ferrocene and the appropriate acyl chloride in solution in dichloromethane in the presence of aluminium chloride (see Part 4<sup>7</sup> for general procedure). Compounds (1a),<sup>10</sup> (1b),<sup>11</sup> (1c),<sup>12</sup> (1e),<sup>13</sup> (1h—j),<sup>14</sup> and (1k)<sup>7</sup> have been described previously. The <sup>1</sup>H n.m.r. spectra of the new compounds (Table 3) were in accord with the structures assigned.

<sup>11</sup> N. Sugiyama, H. Suzuki, Y. Shioura, and T. Teitei, *Bull. Chem. Soc. Japan*, 1962, **35**, 767.

<sup>12</sup> R. J. S. Stephenson, B.P. 846,197 (*Chem. Abs.*, 1961, **35**, 17,647).

<sup>13</sup> F. H. Hon and T. T. Tidwell, *J. Org. Chem.*, 1972, **37**, 1782.

<sup>14</sup> A. W. Baker and D. E. Bublitz, *Spectrochim. Acta*, 1966, **22**, 1787.

*Preparation of Alcohols.*—The alcohols (2a—j), (3a—f), and (4e and k) were prepared by treatment of the ketones (1) in ether solution with lithium aluminium hydride, methyl-lithium, or phenyl-lithium, using standard pro-

cedure to a solution of methylmagnesium iodide (50 mmol) in ether (100 ml). The mixture was heated under reflux for 2 h, cooled, washed (H<sub>2</sub>O), dried (MgSO<sub>4</sub>), and evaporated. The alcohol (5b) (156 mg, 76%) was obtained as a yellow

TABLE 4  
<sup>1</sup>H N.m.r. spectra ( $\tau$  values) of ferrocenylcarbenium ions<sup>a</sup>

Cation	H-2, -5	Ferrocenyl H-3, -4	H-1'-5'	$\overset{+}{\text{C}}\text{H}$ or $\overset{+}{\text{C}}\text{Me}$	Ring Bu <sup>t</sup>	Other
(9a)	4.9—5.05	3.7—3.9	4.78 (s)	2.36 (s)	8.76 (s)	8.51 (s, Bu <sup>t</sup> )
(9b)	4.95—5.0, 5.55—5.85	3.7—3.8	4.82 (s)	2.72 (s)	8.60 (s)	8.55 (s, Bu <sup>t</sup> )
(9c)	4.4—4.5, 5.5—5.6	3.6—3.7	4.8—5.1	2.78 (s)	8.84 (s)	8.55 (s, Bu <sup>t</sup> )
(9d)	5.1—5.2	3.7—3.8	4.3—4.45, 4.75—5.1	2.24 (s)	8.79, 8.81 (2 × s)	8.51 (s, Bu <sup>t</sup> )
(10a)	5.4—5.5	3.6—3.7, 4.05 (t)	5.08 (s)	7.52 (s)	8.62 (s)	7.05—7.45 (CH), 8.45, 8.67 (2 × d, Me)
(10b)	4.95—5.15	3.7—3.8	5.10 (s)	8.03 (s)	8.67 (s)	6.95—7.5 (CH), 8.52, 8.77 (2 × d, Me)
(10c)	4.9—5.25	3.62 (t)	4.9—5.25	8.01 (s)	8.88 (s)	6.95—7.55 (CH), 8.48, 8.72 (2 × d, Me)
(10d)	4.8—5.5	3.5—3.65, 3.85—4.0	4.8—5.5	7.62 (s)	8.62, 8.86 (2 × s)	7.05—7.6 (CH), 8.48, 8.70 (2 × d, Me)
(14a)	5.0—5.1, 5.5—5.6	3.6—3.7	4.78 (s)	2.74 (s)		8.52 (s, Bu <sup>t</sup> )
(14c)	4.8—4.9, 5.25—5.35	3.5—3.7	5.23 (s)	2.35 (s)		2.4—2.7 (Ph), 8.00 (s, Me)
(14e)	4.4—4.5, 5.6—5.7	3.35—3.65	4.92 (s)			2.4—3.1 (Ph), 8.57 (s, Bu <sup>t</sup> )
(14f)	4.25—4.4, 6.2—6.35	3.3—3.45, 3.7—3.9	5.06 (s)	7.64 (s)		2.5—2.95 (Ph), 8.52 (s, Me)
(14g)	5.0—5.1, 5.5—5.6	3.6—3.7	4.78 (s)			8.52 (s, Bu <sup>t</sup> )
(14h)	4.55—4.75	3.5—3.7	5.03 (s)	8.00 (s)		8.50 (s, Bu <sup>t</sup> )
(14i)	4.55—4.75	3.5—3.7	5.03 (s)			8.50 (s, Bu <sup>t</sup> )
(15a)	4.9—5.0	3.5—3.7	5.03 (s)	7.91 (s)		7.0—7.5 (CH), 8.44, 8.69 (2 × d, Me)
(15b)	4.7—4.9, 5.25—5.4	3.55—3.75	5.04 (s)			2.15—3.1 (Ph), 4.79 (s, CH)
(15c)	4.7—4.9	3.5—3.65	5.17 (s)	7.95 (s)		2.4—3.0 (Ph), 4.90 (s, CH)
(15d) <sup>b</sup>	4.45—4.6, 5.45—5.55	3.4—3.6	4.85, 5.01 (2 × s)			2.4—3.1 (Ph), 5.90 (q, CH), 8.02, 8.35 (2 × d, Me)
(15e)	4.45—4.55, 5.25—5.35	3.4—3.5, 3.7—3.8	5.07 (s)	8.15 (s)		2.55—2.75 (Ph), 8.20, 8.33 (2 × s, Me)
(15f)	5.05—5.25	3.5—3.7	5.03 (s)			2.4—3.0 (Ph), 8.06, 8.51 (2 × s, Me)
(15g)	4.9—5.0	3.5—3.7	5.03 (s)	7.91 (s)		8.45br, 8.70br (2 × s, Me)

<sup>a</sup> Trifluoroacetic acid solvent with Me<sub>4</sub>Si as internal reference; integrated relative intensities of signals agreed with the assignments. Only the spectra of those cations which rearrange and their products of rearrangement are given; the spectra of the other cations cited in the text showed no unusual features. <sup>b</sup> Exists in two diastereoisomeric forms.<sup>7</sup>

cedures.<sup>7</sup> Compounds (2a),<sup>10</sup> (2b),<sup>11</sup> (2c),<sup>15</sup> (2e),<sup>13</sup> (2h—j),<sup>14</sup> (3a),<sup>10</sup> (3b),<sup>16</sup> (3c),<sup>13</sup> (3e),<sup>17</sup> (4k),<sup>7</sup> (7a—c),<sup>6</sup> (8a—c),<sup>6</sup> (8d),<sup>5</sup> and (22)<sup>18</sup> have been described previously. The <sup>1</sup>H n.m.r. spectra of the new compounds (Table 3) were in accord with the structures assigned.

The alcohol FcCD(OH)Bu<sup>t</sup> was prepared by reduction of (1e) with lithium aluminium deuteride, and gave a <sup>1</sup>H n.m.r. spectrum identical with that of (2e) except for the lack of the methine proton resonance. The alcohol FcC(OH)(CD<sub>3</sub>)Bu<sup>t</sup> was prepared by the addition of t-butyl-lithium to FcCOCD<sub>3</sub> and gave a <sup>1</sup>H n.m.r. spectrum identical with that of (3e) except for the lack of the methyl proton resonance. These deuteriated compounds, whose m.p.s were close to those of their protio-analogues, were not analysed.

*3-Ferrocenyl-2-methylpropan-2-ol* (5b).—A solution of the ester (5a)<sup>19</sup> (200 mg, 0.8 mmol) in ether (10 ml) was added

solid;  $\tau$  (CDCl<sub>3</sub>) 5.92br (9 H, s, Fc), 7.50 (2 H, s, CH<sub>2</sub>), 8.35br (1 H, s, OH), and 8.90 (6 H, s, Me). Dissolution of this compound in trifluoroacetic acid gave Fc<sup>+</sup>CHPr<sup>i</sup>, identical (<sup>1</sup>H n.m.r.) with that similarly obtained from (2c).

*2-Ferrocenyl-1,1-diphenylethanol* (5c).—The ester (5a) (200 mg, 0.8 mmol) was treated in ether with an excess of phenylmagnesium bromide as in the preceding experiment. The alcohol (5c) (142 mg, 46%) was obtained as a yellow solid;  $\tau$  (CDCl<sub>3</sub>) 2.4—2.9 (10 H, m, Ph), 5.92 (5 H, s, C<sub>5</sub>H<sub>5</sub>), 6.05 and 6.15 (2 H and 2 H, 2 × t, C<sub>5</sub>H<sub>4</sub>), 6.66 (2 H, s, CH<sub>2</sub>), and 7.36br (1 H, s, OH). Dissolution of this compound in trifluoroacetic acid gave Fc<sup>+</sup>CHCHPh<sub>2</sub>, identical (<sup>1</sup>H n.m.r.) with that similarly obtained from (2d).

*2-Ferrocenyl-2-methylpropanoic Acid* (6b).—This compound was obtained (38% yield) from the cyanide (6a) by

<sup>17</sup> M. D. Rausch and C. A. Pryde, *J. Organometallic Chem.*, 1971, **26**, 141.

<sup>18</sup> T. D. Turbitt and W. E. Watts, *Tetrahedron*, 1972, **28**, 1227.

<sup>19</sup> D. T. Roberts, W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, 1967, **89**, 6156.

<sup>15</sup> K. L. Wu, E. B. Sokolova, I. E. Chlenov, and A. D. Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **137**, 111.

<sup>16</sup> H. Egger and K. Schlögl, *J. Organometallic Chem.*, 1964, **2**, 398.

the reported method<sup>20</sup> as yellow needles, m.p. 161—163° (decomp.) (from ether) (lit.,<sup>20</sup> 163—165°);  $\tau$  (CDCl<sub>3</sub>) 5.86br (9H, s, Fc) and 8.55 (6 H, s, Me). This acid decomposes rapidly in ether solution.

*Methyl 2-Ferrocenyl-2-methylpropanoate* (6c).—This ester was prepared (41% yield) from the acid (6b) by the method of Roberts *et al.*<sup>19</sup> and was obtained as yellow needles, m.p. 63—65° (from pentane-ether);  $\tau$  (CDCl<sub>3</sub>) 5.79—5.98 (9 H, m + s, Fc), 6.34 (3 H, s, OMe), and 8.52 (6 H, s, CMe<sub>2</sub>), which slowly decomposed; satisfactory analytical data were not obtained.

*3-Ferrocenyl-2,3-dimethylbutan-2-ol* (6d).—Treatment of the ester (6c) (174 mg, 0.6 mmol) in ether solution with an excess of methylmagnesium iodide was carried out as described for a previous experiment. The alcohol (6d) (143 mg, 82%) was obtained as a yellow solid;  $\tau$  (CDCl<sub>3</sub>) 5.8—6.0 (9 H, m + s, Fc), 8.65 (7 H, s, CMe<sub>2</sub>OH), and 8.98 (6 H, s, CMe<sub>2</sub>). Dissolution of this compound in trifluoroacetic acid gave FcCMeBu<sup>+</sup>, identical (<sup>1</sup>H n.m.r.) with that similarly obtained from the alcohol (3e).

*Carbocation Quenching Experiments*.—The following general procedure was used. The alcohol precursor was dissolved in trifluoroacetic acid giving the appropriate ferrocenylcarbenium ion. The solution was then poured into an excess of saturated aqueous sodium hydrogen carbonate. The products were extracted with ether and separated by column (Al<sub>2</sub>O<sub>3</sub>) or thin-layer chromatography (SiO<sub>2</sub>). In most cases, total product yields were greater than 80%.

(a) From the alcohol (3c), there was obtained *2-ferrocenyl-3-methylbut-1-ene* (11a) (52%), an orange liquid;  $\tau$  (CDCl<sub>3</sub>) 4.70 and 5.00 (1 H, and 1 H, 2 × d, vinyl), 5.55 and 5.75 (2 H and 2 H, 2 × t, C<sub>5</sub>H<sub>4</sub>), 5.90 (5 H, s, C<sub>5</sub>H<sub>5</sub>), 7.0—7.6 (1 H, m, CH), and 8.82 (6 H, d, Me); and the alkene (12a) (26%), orange prisms, m.p. 45—47° (from pentane) (lit.,<sup>13</sup> 46—48.5°);  $\tau$  (CDCl<sub>3</sub>) 5.8—5.9 (9 H, m + s, Fc) and 7.96br and 8.25br (3 H, and 6 H, 2 × s, Me). A small amount of the starting alcohol (3c) was also recovered.

(b) From the alcohol (4e) was obtained an equilibrium mixture of the cations (14e) and (15e) which, on quenching, afforded the starting alcohol (4e) (25%) and *2-ferrocenyl-3-methyl-3-phenylbut-1-ene* (11b) (60%), orange prisms;  $\tau$  (CDCl<sub>3</sub>) 2.56—2.91 (5 H, m, Ph), 4.33 and 4.64 (1 H, and 1 H, 2 × d, vinyl), 6.0—6.25 (9 H, m + s, Fc), and 8.61 (6 H, s, Me).

(c) From the alcohol (2g), there was obtained the cation (14b) which immediately rearranged to the isomer (15b). When the solution was quenched, there was obtained *1-ferrocenyl-1,2,2-triphenylethylene* (12b) (82%), a red solid,  $\tau$  (CDCl<sub>3</sub>) 2.5—3.2 (15 H, m, Ph), 5.93 (5 H, s, C<sub>5</sub>H<sub>5</sub>), and 5.95—6.1 and 6.45—6.6 (2 H and 2 H, 2 × m, C<sub>5</sub>H<sub>4</sub>).

\* Sample kindly donated by Professor R. Dabard.

<sup>20</sup> E. I. Edwards, R. Epton, and G. Marr, *J. Organometallic Chem.*, 1976, **107**, 351.

(d) From the alcohol (8d) was obtained the cation (10d), which rearranged to the cation (9d). When rearrangement was complete (<sup>1</sup>H n.m.r.) the solution was quenched affording *1-(1',2-di-*t*-butylferrocenyl)-2,2-dimethylpropan-1-ol* (7d) (88%), a yellow solid;  $\tau$  (CDCl<sub>3</sub>) 5.45—6.1 (8 H, m, ferrocenyl + CH), 7.90br (1 H, s, OH), and 8.61, 8.79, and 8.82 (each 9 H, 3 × s, Bu<sup>t</sup>).

*3-Ferrocenyl-2-methyl-2-phenylbutane* (13).—Hydrogenation of the alkene (11b) in benzene solution over platinum oxide gave a quantitative yield of *compound* (13), a yellow oil;  $\tau$  (CDCl<sub>3</sub>) 2.80br (5 H, s, Ph), 5.85—6.0 (9 H, m + s, Fc), 7.26 (1 H, q, CH), 8.88 (3 H, d, CHMe), and 8.89br (6 H, s, CMe<sub>2</sub>).

*2,2-Dimethyl[3]ferrocenophan-1-ol* (21).—This alcohol was obtained in quantitative yield by reduction of *2,2-dimethyl[3]ferrocenophan-1-one*<sup>21</sup> with lithium aluminium hydride in ether solution as a yellow solid;  $\tau$  (CDCl<sub>3</sub>) 5.75—6.15 (9 H, m, ferrocenyl + CH), 7.85 and 8.15 (1 H and 1 H, ABq, CH<sub>2</sub>, *J* 15 Hz), 8.32 (1 H, s, OH), and 8.68 and 8.80 (3 H and 3 H, 2 × s, Me).

*2-exo-Methyl-2-phenyl[4](1,2)ferrocenophan-1-ol* (23).—This alcohol was obtained in quantitative yield by reduction of *2-exo-methyl-2-phenyl[4](1,2)ferrocenophan-1-one*<sup>22,\*</sup> with lithium aluminium hydride in ether solution as a yellow-orange solid;  $\tau$  (CDCl<sub>3</sub>) 2.43—2.90 (5 H, m, Ph), 5.7—6.0 (9 H, m + s, ferrocenyl + CH), 7.25—8.2 (5 H, m, CH<sub>2</sub>CH<sub>2</sub> + OH), and 9.02 (3 H, s, Me).

*Rate Measurements*.—The following general procedure was used. A solution of the alcohol precursor (*ca.* 0.2M) in deoxygenated trifluoroacetic acid containing tetramethylsilane as reference was prepared under nitrogen in a sealed n.m.r. tube thermostatted at 328 K or at another desired temperature. The <sup>1</sup>H n.m.r. spectra of these solutions were recorded at appropriate time intervals and the relative proportions of first-formed and rearranged carbenium ions were obtained by integration of suitable well-resolved signals (the C<sub>5</sub>H<sub>5</sub> and Me resonances were particularly useful). The spectra of the cations studied are in Table 4. Reactions were followed over at least three half-lives. First-order rate constants (Table 1) and thermodynamic quantities (Table 2) were calculated conventionally<sup>23</sup> by using least-squares best-fit computer programs. Correlation coefficients better than 0.9995 were obtained and duplicate kinetic runs gave acceptable agreement.

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<sup>21</sup> M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Amer. Chem. Soc.*, 1963, **85**, 316.

<sup>22</sup> H. des Abbayes and R. Dabard, *Tetrahedron*, 1975, **31**, 2111.

<sup>23</sup> A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961.