Stable Carbonium Ions. Part IV.[1] Torsional Barriers in Secondary and Tertiary Ferrocenylalkylium Ions

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Ferrocenylalkylium ions are generated stereospecifically from 1-hydroxyalkylferrocenes in acidic solvents. Using spectroscopic techniques, restricted rotation has been observed for the exocyclic bond of the fulvene ligand of a number of these cations and the height of the torsional barrier has been measured for three systems. In trifluoroacetic acid, the barrier to rotation for a tertiary ferrocenylalkylium ion is lower than that for a secondary ferrocenylalkylium ion which is lower than that for a secondary ruthenocenylalkylium ion. The last cation is configurationally stable at 70°. Restricted ligand torsion has been found for a number of sterically encumbered ferrocenylalkylium ions.

DURING the development of the chemistry of ferrocene, it quickly became apparent that the ferrocenyl group possesses a remarkable electron-releasing capacity.[2]

As one consequence, ferrocenylalkylium ions ($FcCR^1R^2$) † are exceptionally stable species and their intervention dominates much of the organic chemistry of the system.[3] In attempts to account for this enhanced stability and to rationalise the stereospecificity associated with the generation and collapse of these cations (see later), a number of different metal–ligand bonding arrangements have been suggested.

In an early proposal,[4] recently reiterated,[5] Richards suggested that metal–ligand bonding would be optimised if the π-C_5H_5Fe group was displaced intact towards the exocyclic carbon atom (C_{exo}) of the planar fulvene ligand (1). In response to criticism[6] of this model by Rosenblum, it was later suggested[5] that the extent of displacement would be controlled by the electronic nature of the groups attached to C_{exo}. Hisatome and Yamakawa concurred[7] with this concept of a ring-slip structure and further speculated that the location of the (π-C_5H_5Fe) residue with respect to the fulvene ligand might be influenced by the relative steric bulk of the C_{exo}-substituents.

Other structures have been proposed which incorporate an Fe–C_{exo} bond, but in these the fulvene ligand is non-planar. Cais envisaged[3] folding of the ligand across the α-positions (2), arguing that such deformation would permit better overlap between ligand and metal orbitals. From extended Hückel calculations, on the other hand, Gleiter produced[8] an energy-minimum structure (3) in which C_{exo} is displaced from the plane of the adjacent five-membered ring towards the iron atom and in which the rings are tilted. Such out-of-plane deformation has been found[9] in the crystal structure of $(Fc_2CH)^+(BF_4)^-$. However, different bending modes were found for the exocyclic bonds in this cation,

towards the iron atom of one ferrocenyl group and in the opposite direction for the other.

(1)   (2)

(3)   (4)

(5)

Other authors have advocated structures in which bonding between C_{exo} and the iron atom is insignificant. Based upon an analogy with other organometallic cations, Pettit suggested[10] (but later retracted[11]) a structure (4) in which only the α- and β-carbon atoms of the fulvene ligand are bonded to the metal. Traylor also discounted[12] the possibility of Fe–C_{exo} bonding

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† These species could equally well be regarded as (π-cyclopentadienyl)(π-fulvene)iron cations.

[1] Part III, A. M. Easton, M. J. A. Habib, J. Park, and W. E. Watts, *J.C.S. Perkin II*, 1972, 2290.

[2] M. Rosenblum, ' Chemistry of the Iron Group Metallocenes,' Interscience, New York, 1965, Part 1.
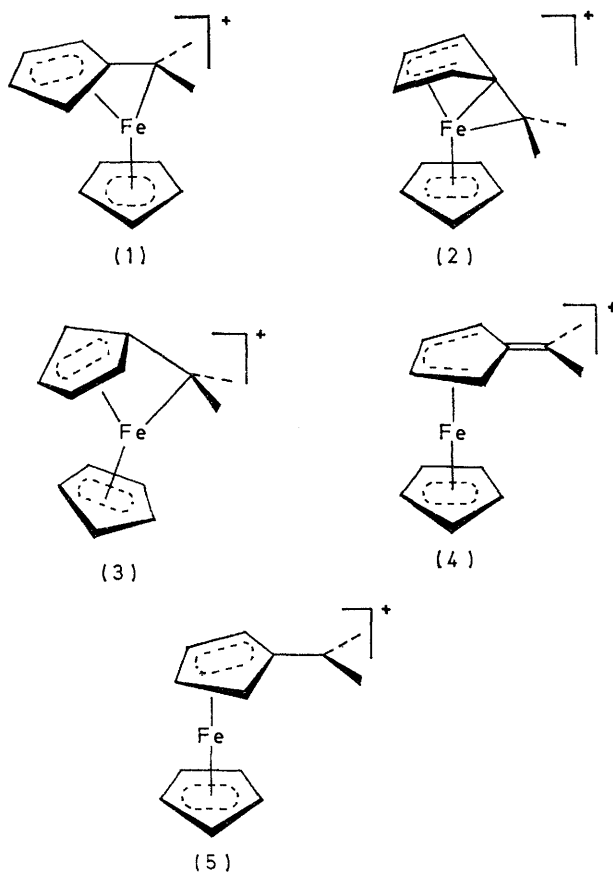
[3] M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435; ' Aromaticity, Pseudo-aromaticity, Anti-aromaticity,' eds. E. D. Bergmann and B. Pullman, Academic Press, New York, 1971.

[4] E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 3840, 4216.

[5] J. J. Dannenberg, M. K. Levenberg, and J. H. Richards, *Tetrahedron*, 1973, **29**, 1575.

[6] J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **91**, 4324.

[7] M. Hisatome and K. Yamakawa, *Tetrahedron*, 1971, **27**, 2101; *Tetrahedron Letters*, 1971, 3533.

[8] R. Gleiter and R. Seeger, *Helv. Chim. Acta*, 1971, **54**, 1217.

[9] S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1025.

[10] J. J. Dannenberg, L. Watts, and R. Pettit, *Tetrahedron Letters*, 1966, 1299.

[11] R. E. Davis, H. D. Simpson, N. Grice, and R. Pettit, *J. Amer. Chem. Soc.*, 1971, **93**, 6688.

[12] T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, 1967, **89**, 2304; T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, 1971, **93**, 5715.

and depicted the system as a resonance hybrid of the canonical structures (4) and (5), with the former regarded as the more important contributor. This iron hyperconjugation formulation was also favoured [13] by Lillya who extended the concept to other carbonium ion systems stabilised by an organometallic group.

In order to gain information bearing upon this problem, we have carried out an extensive study of the properties of ferrocenylalkylium ions. This work is described herein and in the following three papers. Since much of the controversy is concerned with the importance or otherwise of $Fe-C_{exo}$ bonding and with the related question of the degree of double-bond character in the exocyclic bond of the fulvene ligand, we investigated as a first objective the magnitude of the free-energy barrier to rotation around this bond in the system. The results obtained for three amenable cases [(8) $\rightleftharpoons$ (9); (12) $\rightleftharpoons$ (13); (16) $\rightleftharpoons$ (17)] are described in this paper.[14]

From previous work,[4,15] indirect evidence had accumulated to suggest that there is restricted rotation around the exocyclic fulvene bond. For example, it was found [4] that hydrolysis of the acetates of the diastereoisomeric alcohols (6) and (7) proceeds by an S_N1 mechanism with complete retention of configuration, suggesting that the intermediate cations (8) and (9) are generated stereospecifically and do not interconvert prior to stereoselective nucleophilic capture. It also became apparent from these and other studies that, in the formation of a ferrocenylalkylium ion by an ionisation process [equation (1)], it is energetically much

$$FcCR^1R^2X \longrightarrow Fc\overset{+}{C}R^1R^2 + X^- \qquad (1)$$

more favourable for the leaving group (X^-) to depart in the direction away from the iron atom. The stereochemical location of the groups R^1 and R^2 relative to the ferrocenyl residue in cations generated in this way is thus specified by the arrangement of the groups attached to the ionisation site in the precursor.
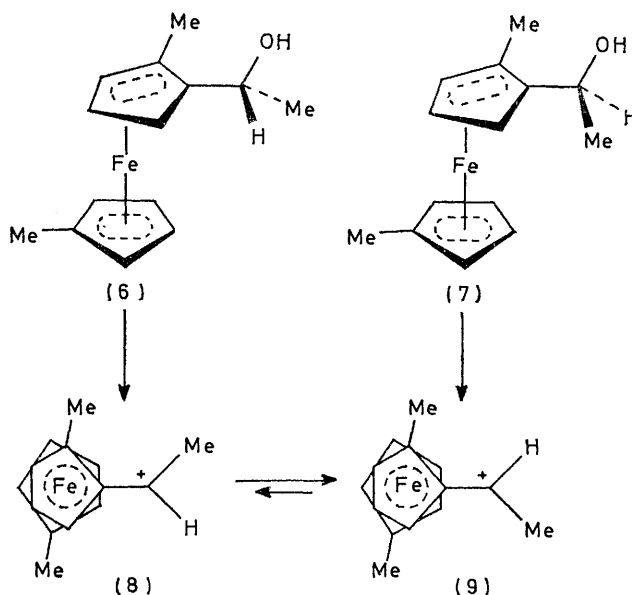
We have found that, in CF_3CO_2H solution, the diastereoisomeric alcohols (6) and (7) do indeed produce different carbonium ions which are clearly differentiated by their [1]H n.m.r. spectra. The spectrum of cation (8), derived from alcohol (6),* changes with time and gives a limiting spectrum which is indistinguishable from that of cation (9) derived from the diastereoisomer (7).* These cations must therefore interconvert by rotation around the (ferrocenyl)-(ĊHMe) bond † giving an equilibrium mixture in which the *anti*-isomer (9) predominates (>97%). The *syn*-isomer (8) is thermodynamically the less stable ($\Delta G^0 > 8\cdot6$ kJ mol^{-1}), pre-

sumably due to steric crowding of the methyl groups attached to the fulvene ligand, and its relative concentration in the equilibrium mixture is below the level of detection by [1]H n.m.r. spectroscopy (*ca.* 3%).

The rate of the isomerisation [(8) $\rightleftharpoons$ (9)] at four temperatures in the range 20—55° was measured by monitoring the rate of disappearance in the spectrum of the ethylidene methyl doublet (τ 7·58) of the less stable cation (8) and the rate of growth of the corresponding doublet (τ 7·77) of its stereoisomer (9). At

each temperature, the kinetic behaviour established the operation of a first-order process. The derived thermodynamic quantities, which relate to the free energy barrier to rotation around the exocyclic bond in the system, are in Table 1.

A different technique was used to measure the torsional barrier associated with the exocyclic bond of the 1-ferrocenylethylium cation [(12) $\rightleftharpoons$ (13)]. The enantiomeric alcohol precursors (10) and (11) were prepared by resolution of 1-ferrocenylethanol according to the reported method.[16] When these enantiomers were dissolved in strongly acidic solvents (*e.g.*, CF_3CO_2H, 60% aqueous H_2SO_4), optically active solutions of the cation were produced. The (R)-(—)-alcohol (10) gave rise to the (+)-cation (12) * while the (S)-(+)-alcohol (11) was converted into the (—)-cation (13).* The initial optical activity of these solutions diminished on standing, inferring racemisation of the substrate by rotation around the exocyclic bond.† The rate of racemisation in CF_3CO_2H was measured at several

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* The stereochemical relationship shown between an alcohol and the derived carbonium ion is based upon the assumption that the leaving group (H_2O) preferentially departs in the direction away from the iron atom (see text).

† When these experiments were conducted in CF_3CO_2D, no H–D exchange of the ethylidene methyl protons was detectable ([1]H n.m.r.) during the period of the isomerisation. This excludes the possibility that the interconversions occur by cation deprotonation to give a vinyl derivative, followed by fast rotation and reprotonation.
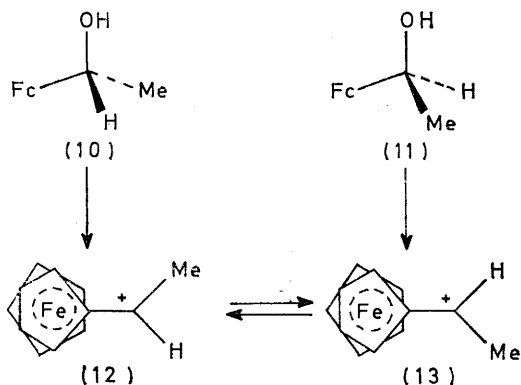
[13] C. P. Lillya and R. A. Sahatjian, *J. Organometallic Chem.*, 1971, **32**, 371.

[14] Preliminary communications: N. M. D. Brown, T. D. Turbitt, and W. E. Watts, *J. Organometallic Chem.*, 1972, **46**, C19; T. D. Turbitt and W. E. Watts, *J.C.S. Chem. Comm.*, 1973, 182.

[15] G. W. Gokel, D. Marquarding, and I. K. Ugi, *J. Org. Chem.*, 1972, **37**, 3052.

[16] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, and I. Ugi, *J. Amer. Chem. Soc.*, 1970, **92**, 5389; G. W. Gokel and I. K. Ugi, *J. Chem. Educ.*, 1972, **49**, 294.

temperatures in the range 40—60° by monitoring the loss of optical activity at 546 and 578 nm (Hg source).

(10) (11)

(12) ⇌ (13)

The same first-order rate constant was calculated for a given temperature irrespective of the wavelength of light or the identity of the chiral cation. From these

ary and tertiary ferrocenylalkylium ions, the [1]H n.m.r. technique was used to study the behaviour of the ferrocenylcyclohexylium cation [(16) ⇌ (17)]. The alcohol precursors (14) and (15) were prepared by addition of ferrocenyl-lithium to 4-t-butylcyclohexanone and were cleanly separated by t.l.c. The major product [(14) : (15) 1 : 2·5] can be assigned structure (15) with an axial hydroxy-group since the operation of either steric-approach or product-development control in the ketone addition reaction would disfavour the production of the equatorial alcohol (14) (cf. ref. 17).

Dissolution of these alcohols in CF_3CO_2H afforded different carbonium ions whose [1]H n.m.r. spectra were clearly distinct. Interconversion of the cations occurred on standing, the equilibrium mixture containing a preponderance (ca. 90%) of the cation (17) derived from the axial alcohol.* The source of the free energy difference (5·9 kJ mol^{-1}) between these stereoisomers may be attributed to a greater steric repulsion between

TABLE 1

Torsional barriers for rotational isomerisation of ferrocenylalkylium ions [a]

Reaction	Temp. (°C) [b]	$10^5 k_f/s^{-1}$	K_{eq}	$E_a/kJ\ mol^{-1}$	$\Delta H^{\ddagger}/kJ\ mol^{-1}$	$T\Delta S^{\ddagger}/kJ\ mol^{-1}$
(8) ⇌ (9)	21·5	1·10	>32			
	30·5	2·97	>32			
	41·5	9·17	>32			
	50·5	26·7	>32	88·7 ± 2·0	86·2 ± 2·0	−14·7 ± 1·5
(12) ⇌ (13)	40·0	4·16	1			
	45·0	7·42	1			
	49·5	10·8	1			
	55·3	18·0	1			
	59·9	26·4	1	84·0 ± 2·0	81·5 ± 2·0	−22·2 ± 1·5
(16) ⇌ (17)	11·5	12·5	12·0			
	19·0	29·7	11·0			
	26·5	61·3	10·5			
	31·0	92·5	10·0	69·4 ± 2·0	66·9 ± 2·0	−17·7 ± 1·5

[a] Thermodynamic quantities refer to the forward reaction; $k_f = k_r K_{eq} = k K_{eq}(1 + K_{eq})^{-1}$; k = apparent rate constant for the forward reaction = $(k_f + k_r)$; E_a, $\Delta H^{\ddagger}$, and $T\Delta S^{\ddagger}$ were calculated conventionally (A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961, 2nd edn.). [b] ±0·5°.

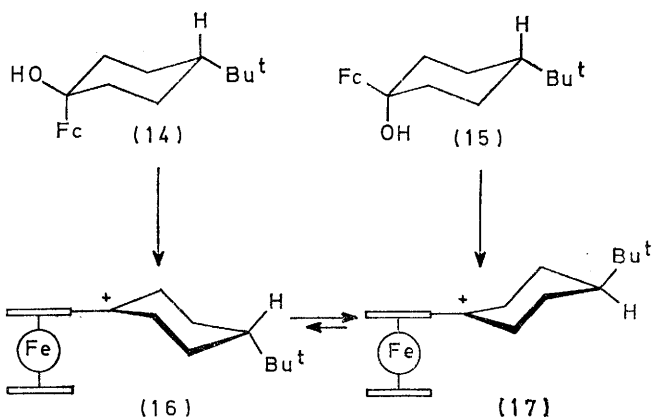results, the free-energy barrier to rotation around the $\overset{+}{Fc-(CHMe)}$ bond was calculated conventionally and the values are in Table 1.

To permit comparison between the properties of a ferrocenylalkylium ion and those of a ruthenium analogue, we carried out an exactly similar study of the torsional barrier in the 1-ruthenocenylethylium cation $(\pi-C_5H_5RuC_5H_4\overset{+}{CHMe})$. The optically active forms of this cation were obtained as before from the enantiomers of 1-ruthenocenylethanol. It was found that solutions of the (+)- and (−)-cations in CF_3CO_2H suffer no loss of optical activity during several days at 70°. This configurational stability points to a torsional barrier greater than ca. 130 kJ mol^{-1}. Since the geometry and dimensions of the ferrocene and ruthenocene molecules are almost identical,[2] the increase in barrier height caused by replacement of iron by ruthenium presumably arises from better overlap between the orbitals of the fulvene ligand and the more extended $4d$ orbitals of the ruthenium atom.

In order to compare the torsional barriers of second-

* See footnote * on page 178.

the conformationally rigid t-butylcyclohexyl ring and the unsubstituted cyclopentadienyl ring in the cation

(14) (15)

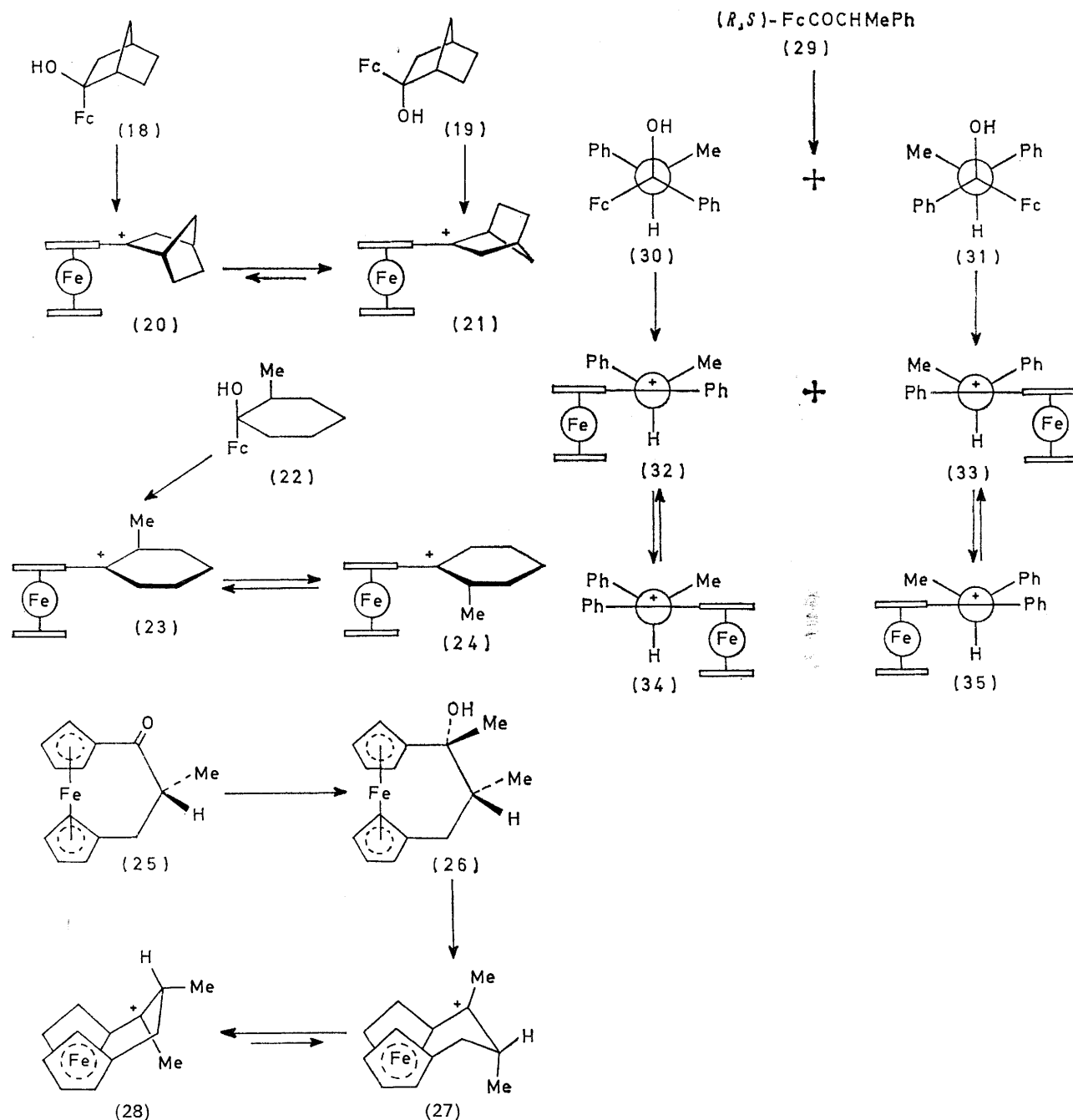(16) (17)

(16) formed from the equatorial alcohol.* The rate of equilibration of the cations in CF_3CO_2H at four temperatures in the range 10—35° was obtained from

[17] H. Falk, H. Lehner, and K. Schlögl, J. Organometallic Chem., 1973, 55, 191.

the rate of growth or decay in the ^{1}H n.m.r. spectrum of the sharp t-butyl singlets characteristic of each species [(16), τ 8·97; (17), τ 9·07]; the operation of a first-order process was again apparent. The derived

double-bond character in the exocyclic bond of the fulvene ligand. The extreme Pettit formulation [10] (4) can therefore be discounted since much higher barriers (typically, 170—200 kJ mol^{-1} for thermal alkene

thermodynamic quantities for the interconversion of the cations are in Table 1.

From the results obtained, the following conclusions can be drawn.

(a) The magnitudes of the torsional barriers (ca. 100 kJ mol^{-1}) show that there cannot be a marked

isomerisations [18]) would be expected for structures incorporating an uncomplexed exocyclic double bond. The same conclusion was reached independently from Mössbauer experiments.[5,19] Similarly, the resonance hybrid representation [(4) ◄► (5)] would appear viable

[18] E. L. Eliel, ' Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 341.

[19] J. J. Dannenberg and J. H. Richards, Tetrahedron Letters, 1967, 4747; cf. R. Gleiter, R. Seeger, H. Binder, E. Fluck, and M. Cais, Angew. Chem. Internat. Edn., 1972, 11, 1028.

only if the contribution of the canonical form (4) is of less importance than considered [12] by Traylor.

(b) In the transition state for rotation, the geometry of the system would preclude bonding between C_{exo} and the iron atom. It may be argued, therefore, that $Fe-C_{exo}$ bonding in the ground state of these cations is either absent or weak (*cf.* crystal structure [9]) since rotation would be prohibited if a strong bond were present.
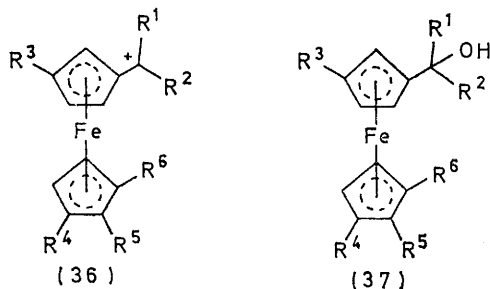
(c) The enthalpy of activation for rotation in the tertiary cation [(16) $\rightleftharpoons$ (17)] is appreciably lower than that for the secondary cation [(12) $\rightleftharpoons$ (13)]. Consequently, the torsional barrier cannot arise principally from steric interaction between a C_{exo}-substituent and the unsubstituted cyclopentadienyl ring in the transition state. If this were so, a higher barrier would be expected for tertiary cations in which C_{exo} bears two alkyl substituents. Increased alkyl electron donation to C_{exo} in the tertiary species, however, would reduce the demand for electron release from the ferrocenyl group. If the source of the barrier were primarily electronic, then a lower barrier would be expected for a tertiary cation, as found experimentally.

Although kinetic investigations were impracticable, we have observed rotational equilibration in a number of other ferrocenylalkylium ion systems using [1]H n.m.r. techniques. Thus, the epimeric 2-ferrocenyl-norbornan-2-ols [20] (18) and (19) in CF_3CO_2H initially gave different cations, (20) [τ 5·04 (s, π-C_5H_5)] and (21) [τ 5·10 (s, π-C_5H_5)] respectively,* which underwent rapid equilibration to give a mixture in which the sterically less crowded isomer (21) largely predominated (*ca.* 95%; *cf.* ref. 19). Similarly, the 1-ferrocenyl-2-methylcyclohexanol isomer (22), which can be obtained pure as the major product of addition of ferrocenyl-lithium to 2-methylcyclohexanone, was converted stereospecifically into the cation (23) [τ 8·63 (d,Me)] * which then underwent equilibration to give a mixture of cations, (23) and (24) [τ 8·23 (d, Me)], in approximately equal proportions.

Two more interesting systems have also been studied. Addition of methyl-lithium to 1,1'-(1-oxo-2-methyltrimethylene)ferrocene [21] (25) gave a single alcohol to which the structure (26) was assigned on consideration of the factors controlling the direction of nucleophilic addition to the carbonyl group of acylferrocenes.[22] In CF_3CO_2H, this alcohol was converted into a single bridged cation [τ 7·15 (s, π-C_5H_5CMe), and 8·36 (d, CMeCH*Me*CH$_2$)] whose stereochemistry (27) may be specified by the preferred orientation of hydroxy-group loss.* Interannular bridge inversion, which is known [23] to occur readily in the 1,1'-trimethylene-

ferrocene system, allows this cation to achieve a more stable conformation (28) [τ 7·24 (s, π-C_5H_5CMe) and 8·72 (d, CMeCH*Me*CH$_2$)] in which steric repulsion between the β-methyl group and the ferrocene residue is relieved. At equilibrium, only the latter conformation was detected in the [1]H n.m.r. spectrum (*i.e.*, >97%).

Treatment of the racemic ketone (29) with phenyl-lithium gave a single racemic diastereoisomeric alcohol to which the (*S*,*R*) and (*R*,*S*) structures (30) and (31) can be assigned from Cram's rule.[24] In CF_3CO_2H, this racemic alcohol was converted stereospecifically into the racemic cation (32; 33) * whose [1]H n.m.r. spectrum [τ 8·02 (d, Me)] attested to its diastereoisomeric purity. Rotational equilibration then occurred generating the other diastereoisomeric cation (34; 35) [τ 8·35 (d, Me)]. At equilibrium, approximately equal proportions of each isomer were present.

a; $R^1 = R^2 = $ Me; $R^3,R^4 = [CH_2]_3$; $R^5 = R^6 = $ H
b; $R^1 = $ Me; $R^2,R^4 = [CH_2]_2$; $R^3 = R^5 = R^6 = $ H
c; $R^1 = R^2 = R^4 = $ Me; $R^3 = R^5 = R^6 = $ H
d; $R^1 = R^2 = $ Me; $R^3 = R^5 = R^6 = $ H; $R^4 = $ Bu^t
e; $R^1 = R^4 = $ Me; $R^2 = $ Bu^t; $R^3 = R^5 = R^6 = $ H
f; $R^1 = R^4 = R^5 = $ Me; $R^2 = $ Bu^t; $R^3 = R^6 = $ H
g; $R^1 = R^4 = R^6 = $ Me; $R^2 = $ Bu^t; $R^3 = R^5 = $ H
h; $R^1 = R^2 = R^4 = R^5 = $ Me; $R^3 = R^6 = $ H
i; $R^1 = R^2 = R^4 = R^6 = $ Me; $R^3 = R^5 = $ H

Relative torsion of the ligands in ferrocenylalkylium ions can also be studied by [1]H n.m.r. spectroscopy.[25] For those cations in which rotation of the rings about the metal–ligand axes is severely restricted by an interannular alkyl bridge [*e.g.*, (27), (28), and (36a, b)], the protons of the alkyl-substituted ring are held in different steric environments with respect to the fulvene ligand and show appreciable [1]H n.m.r. chemical-shift distinction † (Table 2). In the spectra of the unbridged 1'-alkylferrocenylalkylium ions (36c, d), on the other hand, the protons of the (C_5H_4R) ring show very little difference in their chemical shifts and appear, in most cases, as a broadened singlet.[26] It is clear, therefore, that alkyl substituents exert a minimal differential

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* See footnote * on page 178.

† These resonances are readily distinguishable from the resonances due to the ring protons of the fulvene ligand whose chemical shifts conform to a well established pattern (see refs. 5—7).

[20] M. J. A. Habib and W. E. Watts, *J. Chem. Soc. (C)*, 1970, 2552.

[21] T. D. Turbitt and W. E. Watts, *J. Organometallic Chem.*, 1972, **46**, 109.

[22] D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, 1960, no. 13, 1; M. Rosenblum and F. W. Abbate, *J. Amer. Chem. Soc.*, 1966, **88**, 4178; M. J. Nugent and J. H. Richards, *ibid.*, 1969, **91**, 6138; T. D. Turbitt and W. E. Watts, *Tetrahedron*, 1972, **28**, 1227.

[23] T. H. Barr and W. E. Watts, *Tetrahedron*, 1968, **24**, 6111.

[24] D. J. Cram and F. A. Abd Elhafez, *J. Amer. Chem. Soc.*, 1952, **74**, 5828.

[25] Preliminary communication; T. D. Turbitt and W. E. Watts, *J. Organometallic Chem.*, 1973, **49**, C30.

[26] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 189.

effect upon the shieldings of the α- and β-cyclopentadienyl protons. Furthermore, the (C_5H_4R) ring in these cations must be able to rotate freely about the metal–ligand axis such that the magnetic environments of the four ring protons become equivalent on time average.

The protons α and β to the methyl substituent in the (C_5H_4Me) ligand of the cation (36e), however, give rise to two well separated, equally intense multiplets (A_2B_2 pattern) in the spectrum. The rotational freedom of this ligand must therefore be restricted, presumably as a result of steric repulsion between its methyl group and the bulky t-butyl group attached to the fulvene

EXPERIMENTAL

General.—All reactions were carried out under pure, dry N_2. Column chromatography was carried out using Spence Grade H alumina which had been partially deactivated by exposure to the atmosphere for 6 h, analytical and preparative t.l.c. using Merck Kieselgel G, type 60, and g.l.c. using a Perkin-Elmer F11 instrument equipped with an SE 30 column operating at 150—200°. I.r. spectra were recorded for 1% KBr pellets for solids and CCl_4 solutions for liquids using a Perkin-Elmer 457 spectrometer, electronic spectra for EtOH solutions (unless otherwise stated) using a Unicam SP 800A spectrometer, and ^1H n.m.r. spectra for $CDCl_3$ (neutral compounds) or CF_3-CO_2H (cations) solutions as indicated using Perkin-Elmer

TABLE 2
^1H n.m.r. spectra of ferrocenylalkylium ions [a]

Cation	Alkyl resonances (τ) [b]			Cyclopentadienyl resonances (τ) [b,c]		
	(R_2C^+)	1'-Alkyl		α-H	β-H	1'-H
(16)	7·2—8·4 (cyclohexyl), 8·97 (s, Bu^t)			4·93	3·70	4·89 (s)
(17)	7·2—8·4 (cyclohexyl), 9·07 (s, Bu^t)			5·09	3·75	5·17 (s)
(20)	6·7—8·5 (norbornyl)			5·00	3·70	5·04 (s)
(21)	6·7—8·5 (norbornyl)			5·00	3·70	5·10 (s)
(23)	7·4—8·2 (cyclohexyl), 8·63 (d, Me)			4·95	3·65	4·91 (s)
(24)	7·0—8·5 (cyclohexyl), 8·23 (d, Me)			4·95	3·65	5·05 (s)
(27)	7·15 (s, Me), 5·8—6·5 ($CHCH_2$), 8·36 (d, Me)			d	d	d
(28)	7·24 (s, Me), 5·8—7·1 ($CHCH_2$), 8·72 (d, Me)			d	d	d
(32; 33)	2·4—3·1 (Ph), 5·90 (q, CH), 8·02 (d, Me)			4·51, 5·47	3·52	4·85 (s)
(34; 35)	2·4—3·1 (Ph), 5·90 (q, CH), 8·35 (d, Me)			4·50, 5·50	3·50	5·01 (s)
(36b)	7·14 (s, Me), 5·9—6·35 (CH_2)	6·7—7·3 (CH_2)		d	d	d
(36e)	8·02 (s, Me), 8·48 (s, Bu^t)	8·27 (s, Me)		4·55—4·75	3·65	4·85 (2H), 5·21 (2H)
(36f)	8·08 (s, Me), 8·53 (s, Bu^t)	8·34 (s, Me)		4·15	3·88	4·78 (1H), 5·07 (2H)
(36g)	8·20 (s, Me), 8·53 (s, Bu^t)	8·30 (s, Me)		4·65, 4·85	3·60, 3·80	4·95 (2H), 5·50 (1H)

[a] For CF_3CO_2H solutions with Me_4Si as internal reference. The spectra of the other cations cited in this paper are given in ref. 26. [b] Integrated relative intensities agreed with the proton assignments; multiplets unless indicated otherwise; (s) singlet, (d) doublet, (q) quartet. [c] The location of the ring protons relative to the (R_2C^+) substituent is given. [d] Ring proton resonances appear as a complex pattern in the range τ 3·4—5·4.

ligand. If the fulvene ligands of ferrocenylalkylium ions were planar, it seems unlikely that the barrier to ligand rotation in cation (36e) would be significantly higher than that in its isomer (36d) for which, as indicated previously, there is no indication of restricted ligand torsion. However, if the fulvene ligands were distorted in the manner suggested by Cais [3] (2) or Gleiter [8] (3), stereomodel measurements show that the rotation of the (C_5H_4R) ligand would be more impeded in cation (36e) than in its isomer (36d), in accord with the spectroscopic behaviour.

Evidence of restricted ligand rotation in other t-butyl-substituted cations has been obtained. For example, the ring protons of the ($C_5H_3Me_2$) ligands in cations (36f, g) give rise to two ^1H n.m.r. multiplets. The corresponding protons of cations (36h, i), in which the rotation of the ($C_5H_3Me_2$) ring is unimpeded, on the other hand, produce a broadened singlet.[26] From the relative intensities and chemical shifts of the ring proton resonances in the spectra of the cations of the former pair (Table 2), it can be seen that the lower-field resonances correspond to those ring protons which spend a greater proportion of their time directly beneath C_{exo} of the fulvene ligand.

R10 and R12A spectrometers operating at 60 MHz with Me_4Si as internal reference. Optical rotations were measured using a Perkin-Elmer 141 digital polarimeter. Alkyl- and aryl-lithium reagents were used as supplied by Alfa Inorganics. Light petroleum refers to the fraction of b.p. 40—60°. Microanalyses were carried out by the Alfred Bernhardt Microanalytical Laboratory, Mulheim, West Germany. Yields of products are based on unrecovered starting material.

Preparation of Ketones.—Except for the compound whose preparation is given below, all the ketones required in this study have been described elsewhere (see ref. 26).

(R,S)-(2-*Phenylpropionyl*)*ferrocene* (29).—A solution of 2-phenylpropionyl chloride (3·4 g, 0·02 mol) in CH_2Cl_2 (10 ml) was added dropwise to a mixture of ferrocene (3·7 g, 0·02 mol) and $AlCl_3$ (2·6 g, 0·02 mol) in CH_2Cl_2 (50 ml) at 0°. The mixture was stirred and allowed to reach room temperature during 4 h and then stirred overnight. The mixture was poured into water and the organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in light petroleum and chromatographed. This solvent eluted unchanged ferrocene (1·3 g, 30% recovery). Light petroleum–ether (2 : 1) eluted the *ketone* (29) (2·1 g, 50%), an orange solid, m.p. 95—97° (Found: C, 71·7; H, 5·7. $C_{19}H_{18}FeO$ requires C, 71·7; H, 5·7%); τ 2·67br (5H, s, Ph), 5·20 and

5·55 (2 × 2H, 2 × m, C₅H₄), 5·75 (1H, q, CH), 5·97 (5H, s, π-C₅H₅), and 8·50 (3H, d, Me).

5·55 (2 × 2H, 2 × m, C_5H_4), 5·75 (1H, q, CH), 5·97 (5H, s, π-C_5H_5), and 8·50 (3H, d, Me).

TABLE 3

Alcohols

Compd.	M.p. (°C) [a]	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
(14)	91—93	$C_{20}H_{28}FeO$	70·5	8·4	70·6	8·3
(15)	108—110	$C_{20}H_{28}FeO$	70·4	8·4	70·6	8·3
(22)	83—85	$C_{17}H_{22}FeO$	68·2	7·5	68·5	7·4
(26)	43—44	$C_{15}H_{18}FeO$	66·5	6·7	66·7	6·7
(30; 31)	102—104	$C_{25}H_{24}FeO$	75·7	5·9	75·8	6·1
(37b)	113—115 [b]	$C_{14}H_{16}FeO$				
(37e)		$C_{17}H_{24}FeO$	67·8	8·2	68·0	8·1
(37f)	58—60	$C_{18}H_{26}FeO$	68·9	8·1	68·8	8·3
(37g)		$C_{18}H_{26}FeO$	68·5	8·2	68·8	8·3

[a] Unless liquid. [b] Lit.,[27] 114·5—115·5°.

Preparation of Alcohols.—Hydride reductions. 1-Ferrocenylethanol, 1-ruthenocenylethanol, and the diastereoisomeric alcohols (6) and (7) were prepared by $LiAlH_4$ reduction of the corresponding ketones according to reported methods (see ref. 4).

Methyl-lithium additions. The alcohols (37a—d, h, i), which have been described elsewhere (see refs. 26 and 27), were prepared by the addition of methyl-lithium to the corresponding ketones.

1,1′-(1-Hydroxy-trans-1,2-dimethyltrimethylene)ferrocene (26). A solution of the ketone [21] (25) (0·25 g, 0·001 mol) in ether (20 ml) was added slowly to an excess of methyl-lithium in ether (30 ml) and the mixture was stirred for 1 h. The excess of methyl-lithium was destroyed (EtOH) and the mixture was poured into water. The organic 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 a single yellow band which afforded the pure *alcohol* (26) (0·25 g, 100%), a yellow solid, m.p. 43—44°; τ 5·73, 6·00, and 6·15 (8H, 3 × m, ferrocenyl), 7·95 (3H, m, bridge), 8·15 (1H, s, OH), 8·53 (3H, s, C*Me*OH), and 8·85 (3H, d, CH*Me*). Analytical results are in Table 3.

t-Butyl-lithium additions. The alcohols (37e—g) were prepared by the addition of t-butyl-lithium to the corresponding ketones as described below for a typical experiment. Analytical data, etc., are in Table 3.

3,3-Dimethyl-2-(1-methylferrocenyl)butan-2-ol (37e). A solution of 1-acetyl-1′-methylferrocene [26] (0·24 g, 0·001 mol) in ether (50 ml) was stirred under N_2 and an excess of t-butyl-lithium (2M in hexane) (**caution!** inflammable in air) was added by syringe through a septum cap. The mixture was stirred for 1 h and then the excess of t-butyl-lithium was destroyed (MeOH). The mixture was poured into water, and the organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. Chromatography of the residue in light petroleum–ether (3 : 1) afforded as the sole product the *alcohol* (37e) (0·27 g, 90%), a yellow liquid; τ 5·8—6·1 (8H, m, ferrocenyl), 8·01 (3H, s, ring Me), 8·05 (1H, s, OH), 8·41 (3H, s, C*Me*OH), and 9·15 (9H, s, Bu^t).

Ferrocenyl-lithium additions. The preparations of the epimeric alcohols (18) and (19) were previously reported.[20]

4-t-Butyl-1-ferrocenylcyclohexanols (14) *and* (15). A solution of ferrocene (3·7 g, 0·02 mol) in tetrahydrofuran (20 ml) was added to a solution of butyl-lithium (20 ml; 1M in ether–hexane) and the mixture was stirred for 6 h.

A solution of 4-t-butylcyclohexanone (3·0 g, 0·02 mol) in tetrahydrofuran (10 ml) was then added and the mixture was stirred overnight. Methanol (3 ml) was added and the mixture was poured into water and extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was dissolved in ether and chromatographed. Light petroleum eluted unchanged ferrocene (1·3 g, 35% recovery). Light petroleum–ether (3 : 1) eluted a single yellow band which afforded a mixture of the alcohols (14) and (15). The ^1H n.m.r. spectrum of the total product mixture was recorded. The mixture was separated by preparative t.l.c., using light petroleum–ether (9 : 1) as eluant. The less polar alcohol (15) was obtained as a yellow solid, m.p. 108—110° (lit.,[17] 106—108°), τ 5·80 (9H, m, ferrocenyl), 8·0—8·6 (9H, m, cyclohexyl), 8·25 (1H, s, OH), and 9·10 (9H, s, Bu^t). The more polar alcohol (14) was obtained as a yellow solid, m.p. 91—93° (lit.,[17] 98—100°), τ 5·70 (9H, m, ferrocenyl), 7·9—8·6 (9H, m, cyclohexyl), 7·40 (1H, s, OH), and 9·20 (9H, s, Bu^t). The ^1H n.m.r. spectrum of the original mixture showed that these alcohols (14) and (15) were formed in the ratio 1 : 2·5 respectively (relative heights of Bu^t singlets). Analytical data are in Table 3.

trans-1-Ferrocenyl-2-methylcyclohexanol (22). A solution of lithiated ferrocene was prepared from ferrocene (3·7 g, 0·02 mol) as described above. A solution of 2-methylcyclohexanone (2·2 g, 0·02 mol) in tetrahydrofuran (10 ml) was added and the mixture was stirred overnight. Methanol (3 ml) was added and the reaction was worked-up as described above. The residue was chromatographed. Light petroleum eluted unchanged ferrocene (1·1 g, 30% recovery). Light petroleum–ether (3 : 1) eluted the *alcohol* (22) (4·0 g, 65%), a yellow solid, m.p. 83—85°, τ 5·80 (9H, m, ferrocenyl), 8·05 (1H, s, OH), 8·1—8·6 (9H, m, cyclohexyl), and 8·50 (3H, d, Me). Analytical results are in Table 3. Small amounts of other products were not investigated.

(S,R; R,S)-1-*Ferrocenyl-1,2-diphenylpropan-1-ol* (30; 31). A slight excess of phenyl-lithium (2M in benzene–ether) was added to a solution of the racemic ketone (29) (0·64 g, 0·002 mol) in ether (50 ml) and the mixture was stirred overnight. The reaction was worked-up as described for the methyl-lithium additions. The sole product obtained after column chromatography and t.l.c. was the racemic *diastereoisomer* (30; 31) (0·62 g, 77%), a yellow solid, m.p. 102—104°; τ 2·2—2·7 (5H, m, Ph), 2·80 (5H, s, Ph), 6·05 and 6·60 (4H, 2 × m, C_5H_4), 6·17 (5H, s, π-C_5H_5), 7·41 (1H, s, OH), 8·50 (1H, m, CH), and 8·83 (3H, d, Me). Analytical results are in Table 3.

Resolution of Alcohols.—Racemic 1-ferrocenylethanol was resolved according to the reported method.[16] The (R)-(—)-enantiomer (10) gave $[\alpha]_D^{25}$ —20·1° (c 1·5, C_6H_6) (66% optical purity) and the (S)-(+)-enantiomer (11) gave $[\alpha]_D^{25}$ +8·5° (c 1·5, C_6H_6) (28% optical purity).

NN-Dimethyl-1-ruthenocenylethylamine. 1-Ruthenocenylethanol was resolved by the following sequence. The racemic alcohol [4] (1·3 g, 0·005 mol) in 1,2-dichloroethane (20 ml) was added to a stirred solution of aluminium chloride (1·3 g, 0·01 mol) and dimethylamine (0·45 g, 0·01 mol) in 1,2-dichloroethane (30 ml). The mixture was stirred for 1 h at room temperature and then poured into aqueous H_2SO_4 (0·05M, 200 ml). The acidic layer was

[27] M. Hisatome and K. Yamakawa, *Tetrahedron Letters*, 1971, 3533.

washed with ether, then neutralised (0·1M-NaOH), and extracted with ether. The extract was washed (H$_2$O), dried (MgSO$_4$), and evaporated giving the title *amine* (1·4 g, 93%), a yellow liquid (Found: C, 55·6; H, 6·1; N, 4·5. C$_{14}$H$_{19}$NRu requires C, 55·6; H, 6·3; N, 4·6%), τ 5·45 (9H, m, ruthenocenyl), 6·64 (1H, q, CH), 7·84 (6H, s, NMe$_2$), and 8·74 (3H, d, Me).

A solution of this amine (1·4 g, 0·005 mol) in methanol (3 ml) at 55° was mixed with a solution of (+)-tartaric acid (0·75 g, 0·005 mol) in methanol (3 ml) at 55° and the resulting solution was allowed to cool very slowly overnight. The amine tartrate, which had crystallised from solution (0·9 g), was dissolved in aqueous NaOH (20%) and the solution was extracted with CH$_2$Cl$_2$. The extract was washed (H$_2$O), dried (K$_2$CO$_3$), and evaporated, yielding a sample (0·55 g) containing an excess of the (−)-amine, $[\alpha]_D^{25}$ −12·0° (*c* 1·0, EtOH). Evaporation of the mother liquor from the above crystallisation gave a further sample (1·2 g) of amine tartrate. Treatment with base as above liberated the amine (0·8 g) containing an excess of the (+)-enantiomer $[\alpha]_D^{25}$ +8·0° (*c* 1·0, EtOH). The optical purity of these amine samples was not determined.

Each of the optically active amine samples from the preceding experiment was quaternised (MeI in ether). The resulting quaternary salts were hydrolysed in refluxing tetrahydrofuran–water (1 : 1) and the corresponding alcohols were recovered by ether extraction. The (−)-amine gave (+)-1-ruthenocenylethanol $[\alpha]_D^{25}$ +20·7° (*c* 1·5, C$_6$H$_6$), while the (+)-amine gave (−)-1-ruthenocenylethanol, $[\alpha]_D^{25}$ −13·1° (*c* 1·5, C$_6$H$_6$). The optical purity of these alcohols is unknown.

Preparation of Carbonium Ions.—Samples of the alcohols were dissolved in CF$_3$CO$_2$H (*ca.* 50 g l^{-1}) giving quantitatively the corresponding carbonium ions whose ^{1}H n.m.r. spectra are summarised in Table 2 and in Part VI.[26] The spectra of the cations obtained from the alcohols (7) and (10) in CF$_3$CO$_2$D were identical with those obtained using CF$_3$-CO$_2$H as solvent. No H–D exchange of the ethylidene methyl protons of (9) or (12) was detected during several hours at 33°, nor during the isomerisation of (8) to (9).

Solutions of the cations (12) and (13), obtained from optically active samples of 1-ferrocenylethanol in CF$_3$CO$_2$H (*c* 0·1) were optically active. An enantiomeric excess of the (−)-alcohol (10) produced an excess of the (+)-cation (12); $[\alpha]_{589}^{25}$ +395°, $[\alpha]_{578}^{25}$ +310°, $[\alpha]_{546}^{25}$ +475°. An enantiomeric excess of the (+)-alcohol (11) produced an excess of the (−)-cation (13); $[\alpha]_{589}^{25}$ −395°, $[\alpha]_{578}^{25}$ −310°, $[\alpha]_{546}^{25}$ −475°. Rotations given are calculated for 100% optically pure alcohols and are considered accurate to ±10°.

Solutions of optically active samples of 1-ruthenocenyl-ethanol in CF$_3$CO$_2$H (*c* 0·1) were optically active. The (+)-alcohol sample, $[\alpha]_{589}^{25}$ +20·7°, gave the (−)-cation; $[\alpha]_{546}^{25}$ −110°, $[\alpha]_{578}^{25}$ −98°, $[\alpha]_{589}^{25}$ −90°. The (−)-alcohol sample, $[\alpha]_{589}^{25}$ −13·1°, gave the (+)-cation; $[\alpha]_{546}^{25}$ +70°, $[\alpha]_{578}^{25}$ +63°, $[\alpha]_{589}^{25}$ +57°. The optical

activity of these solutions was unchanged after several days at 70° in a sealed tube.

Kinetic Methods.—^{1}H N.m.r. studies. (a) (8) ⇌ (9). A solution of the cation (8) was prepared by dissolving the alcohol (6) in CF$_3$CO$_2$H (*ca.* 50 g l^{-1}). The solution was transferred to a sealed n.m.r. tube, thermostatted at 21·5°, and the spectral range τ 6—10 scanned at regular time intervals until the methyl doublet resonance of (8) at τ 7·50 (*J* 7·5 Hz) had been replaced by the corresponding doublet of (9) at τ 7·72 (*J* 7·5 Hz). Two runs gave good agreement. The process was repeated at 30·5, 41·5, and 50·5°. The relative proportions of (8) and (9) present at each observation were calculated from the relative peak heights of the corresponding resonances, which were equally sharp (identical width : half-height ratios). The rate constant for the isomerisation at each temperature was obtained from a plot of log $[A]_t$ vs. time, where $[A]_t$ = concentration of (8) at time t. A good linear relationship obtained (correlation coefficient >0·95). The presence of (8) in the equilibrium mixture was not detected (*i.e.*, <3%). The rate constants obtained are in Table 1.

(b) (16) ⇌ (17). This isomerisation was similarly monitored at 11·5, 19·0, 26·5, and 31° by observing the rate of growth and decay of the equally sharp t-butyl singlet resonances of the species (Table 2). The rate constants for the forward reaction, k_f, were obtained from plots of log $\{[A]_t − [A]_e\}$ vs. time, where $[A]_t$ and $[A]_e$ refer to the concentrations of (16) at time t and at equilibrium respectively. Good linear relationships were obtained. The equilibrium constant, K_{eq}, for each temperature was calculated from the relative concentrations of (16) and (17) when spectral change had ceased. The same equilibrium mixtures were formed from both (16) and (17). The results are in Table 1.

Optical rotation studies. Optically active solutions of the 1-ferrocenylethyl cation [(12) + (13)] were prepared from optically-active samples of the alcohols [(10) + (11)] in CF$_3$CO$_2$H (*ca.* 1·0 g l^{-1}). The rate of loss of optical activity of these solutions at 40, 45, 49·5, 55·3, and 59·9° was followed using a thermostatted polarimeter (10 cm closed cell) operating at 546 and 578 nm. The rate constant for racemisation, $k = (k_f + k_r)$ for (12) ⇌ (13), at each temperature was obtained from a plot of log R_t vs. time, where R_t = optical rotation of solution at time t. Good linear relationships were observed. Within experimental error, the same rate constant was calculated for a given temperature irrespective of the alcohol sample used [excess (+)- or (−)-enantiomer] or the wavelength of light selected. The results are in Table 1.