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Preliminary communication

Torsional barriers in ferrocenylcarbonium ions

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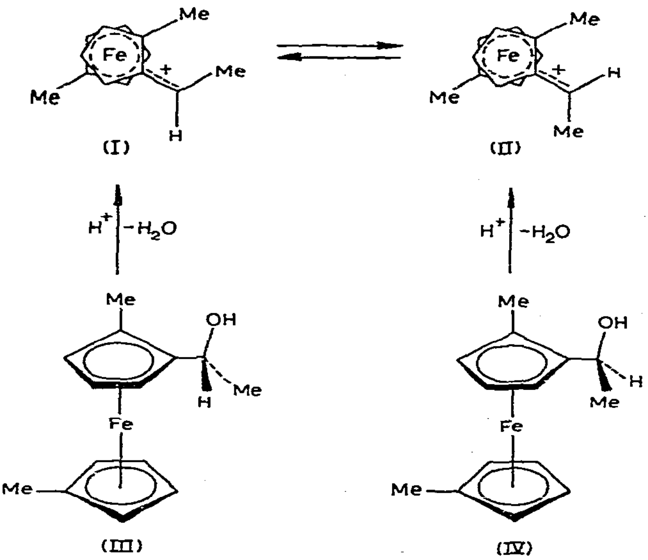
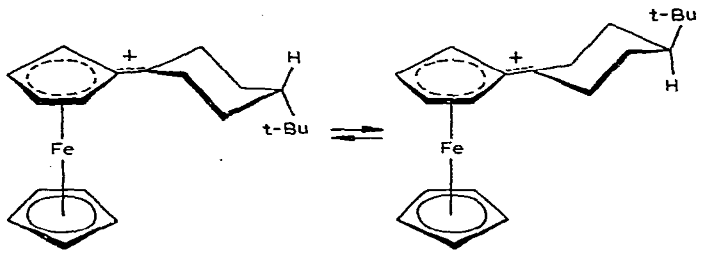
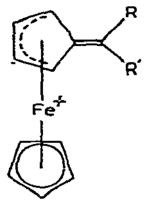
Although a number of structural models have been proposed[1-5] for ferrocenylcarbonium ions (alternatively, π-cyclopentadienyl-π-fulveneiron cations), uncertainty still exists concerning the nature of the bonding arrangement between the iron atom and the fulvene ligand. Since the magnitude of the free-energy barrier to rotation around the bond connecting the ferrocenyl group and the exocyclic carbon atom should reflect the electronic structure of the species, we have determined the free-energy of activation for this process in two amenable cases, (I) → (II) and (V) → (VI).

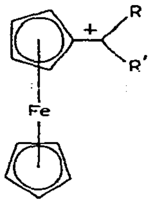




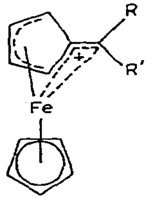
(V) (VI)



(VII)



(VIII)



(IX)

Solvolysis studies[1] have established that, in the formation of a ferrocenylcarbonium ion by an S_N1-ionisation process, it is energetically much more favourable for the leaving-group to depart in an *exo*-direction (*i.e.* away from the iron atom). Accordingly, the secondary cation (I) is formed stereospecifically when the alcohol (III)★ is dissolved in CF_3CO_2H, while the diastereoisomeric alcohol (IV)★ is similarly converted to the stereoisomeric cation (II). These cations, which give distinctive ^{1}H NMR spectra in CF_3CO_2H, may be interconverted by rotation around the ferrocenyl–(CHMe) bond★★. The former is thermodynamically the less stable ($\Delta G^\circ > 8.6$ kJ·mol^{-1}), presumably due to steric crowding of the methyl groups, and its relative concentration in the equilibrium mixture is below the level of detection by ^{1}H NMR spectroscopy. Under the operating conditions, a concentration > 3% (relative to that of the major isomer) would be detectable.

The rate of the isomerisation (I) → (II) at four temperatures (in the range 20–55°) was measured by monitoring the rate of disappearance in the ^{1}H NMR spectrum of the ethylidene methyl doublet (τ 7.50; J = 7.5 Hz) of the less stable cation (I) and the rate of growth of the corresponding doublet (τ 7.72; J = 7.5 Hz) of its stereoisomer (II). At each temperature, the kinetic behaviour was in excellent accord with the operation of a first-order process.

A similar investigation of the equilibration of the stereoisomeric tertiary cations (V) and (VI) was also carried out. The latter predominated at equilibrium (ΔG° = 5.9 kJ·mol^{-1}). As in the previous case, these cations were formed stereospecifically from the isomeric

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★ The structures of these alcohols were established by Hill and Richards[1].

★★ When the experiment is conducted in CF_3CO_2D solvent, no H/D exchange of the ethylidene methyl protons is detected during the period of the isomerisation. This excludes the possibility that the transformation occurs by deprotonation to give a vinylferrocene followed by fast rotation and reprotonation.

4-t-butyl-1-ferrocenylcyclohexanols★ in CF_3CO_2H. The rate of equilibration at four temperatures (in the range 10—35°) was obtained from the rate of growth or decay in the ^1H NMR spectrum of the sharp t-butyl singlets characteristic of each species [(V), τ 8.97; (VI), τ 9.07]. The operation of a first-order process was again established.

TABLE 1

Equilibration reaction	*Temp.* ^{a} *(°C)*	10^5 k_f ^{b} *(s^{-1})*	$K_{eq.}$	$\Delta H^{\ddagger}$ ^{c} *($kJ \cdot mol^{-1}$)*	$\Delta S^{\ddagger}$ ^{c} *($J \cdot mol^{-1} \cdot deg^{-1}$)*
(I) $\underset{k_r}{\overset{k_f}{\rightleftarrows}}$ (II)	21.5	1.10	> 32		
	30.5	2.97	> 32		
	41.5	9.17	> 32		
	50.5	26.7	> 32		
				86.2 ± 2.0	− 49
(V) $\underset{k_r}{\overset{k_f}{\rightleftarrows}}$ (VI)	11.5	12.5	12		
	19.0	29.7	11		
	26.5	61.3	10.5		
	31.0	92.5	10		
				66.9 ± 2.0	− 59

^{a} ± 0.5°. ^{b} $k_f = k_r K_{eq.} = k K_{eq.} (1 + K_{eq.})^{-1}$; k = apparent rate constant for the forward reaction = $(k_f + k_r)$. ^{c} For the forward reaction.

Rate constants and derived thermodynamic quantities for the two reactions are given in Table 1. Two important conclusions may be drawn from these data. Firstly, the 16-electron formulation (VII)[3] can be discounted for these cations since much higher torsional barriers would be required for structures incorporating an uncomplexed exocyclic carbon—carbon double bond. The results obtained do not permit a decision between a resonance-hybrid formulation [(VII) ↔ (VIII)][4] or structures of the type (IX)[1] in which the fulvene ligand may be distorted from planarity[2,5]. Secondly, the large difference in enthalpy of activation found for rotation in the cations (I) and (V) suggests that there may be appreciable differences in the metal—ligand bonding in tertiary ($\text{Fc}\overset{+}{\text{C}}\text{RR}'$), secondary ($\text{Fc}\overset{+}{\text{C}}\text{HR}$) and, by extrapolation, in primary ($\text{Fc}\overset{+}{\text{C}}\text{H}_2$) ferrocenylcarbonium ions.

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★ These alcohols, which were prepared by the reaction of ferrocenyllithium with 4-t-butylcyclohexanone, were satisfactorily characterised.