Direct Observation of an Optically-active Carbonium Ion and Measurement of the Free-energy Barrier to Racemisation

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Summary Both (+)- and (−)- forms of the 1-ferrocenylethyl cation have been generated in acidic solvents from alcohol precursors and the free-energy barrier to rotation around the $\mathrm{Fc{-}\overset{+}{C}HMe}$ bond has been determined.

IT has been inferred from previous studies[1,2] that, in the formation of a ferrocenylcarbonium ion by an S_N1-ionisation process [equation (1)], it is energetically much more

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

favourable for the leaving-group ($\mathrm{X^-}$) to depart in an *exo*-direction (*i.e.* away from the iron atom). In consequence, the stereochemical location of the groups R^1 and R^2 relative to the ferrocene unit in cations generated in this way is specified by the arrangement of the groups attached to the ionisation site in the precursor molecule. Recently, it has also been shown[3] that there exists an appreciable energy barrier to rotation around the bond connecting the ferrocenyl group and the formal positive centre in cations of this type.

Accordingly, we have found that dissolution of (*R*)-(−)-1-ferrocenylethanol (**1**)† in acidic solvents (*e.g.* $\mathrm{CF_3CO_2H}$, 60% $\mathrm{H_2SO_4}$ aq.) produces an optically-active form (**3**) of the 1-ferrocenylethyl cation $\{[\alpha]_D^{25} = +395°$ ($c = 0{\cdot}1$ in $\mathrm{CF_3CO_2H}$)$\}$. Similarly, the (*S*)-(+)-enantiomer (**2**)† of the alcohol is converted into the stereoisomeric (−)-carbonium ion (**4**) $\{[\alpha]_D^{25} = -395°$ ($c = 0{\cdot}1$ in $\mathrm{CF_3CO_2H}$)$\}$.

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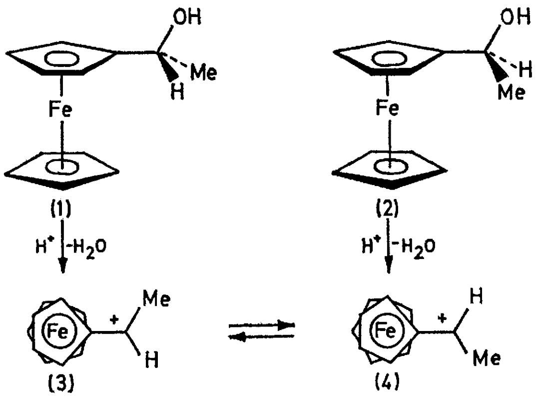
† These optical isomers were prepared by the method of resolution devised by Ugi *et al.* (refs. 2,4).



These chiral cations interconvert slowly by rotation around the exocyclic bond and thereby suffer racemisation.‡ Within experimental error, the same first-order rate constant for racemisation§ ($8{\cdot}32 \times 10^{-5}$ s^{-1} in CF_3CO_2H at 40°) was calculated for a given temperature (in the range 40—60°) irrespective of the wavelength of the light used (546, 578, and 589 nm) or the identity of the chiral cation. The derived thermodynamic quantities ($\Delta H^{\ddagger} = 81{\cdot}5$ kJ mol^{-1}; $T\Delta S^{\ddagger} = -22{\cdot}2$ kJ mol^{-1}), which constitute the free-energy barrier to rotation around the $\mathrm{Fc\text{–}\overset{+}{C}HMe}$ bond, agree well with results previously obtained[3] using ^1H n.m.r. techniques for the rotational barrier in a related secondary ferrocenylcarbonium ion.

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‡ The methyl protons of the 1-ferrocenylethyl cation do not undergo H–D exchange in CF_3CO_2D solution (^1H n.m.r.). Interconversion of the cations (**3**) and (**4**), therefore, does not occur by a deprotonation–reprotonation mechanism involving vinylferrocene.

§ The rate constant for racemisation is twice that for the equilibration of the cations.

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