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Preliminary communication

Double-shift rearrangements of secondary ferrocenylcarbonium ions

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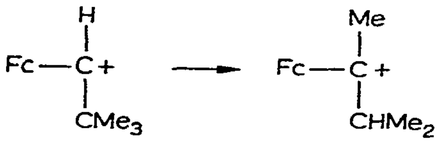
SUMMARY

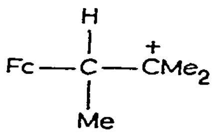
In CF_3CO_2H solution, secondary ferrocenylcarbonium ions ($\mathrm{Fc\overset{+}{C}HCR^1R^2R^3}$) undergo a quantitative double-shift rearrangement to generate isomeric tertiary carbonium ions ($\mathrm{Fc\overset{+}{C}R^1CHR^2R^3}$).

Ferrocenylcarbonium ions ($\mathrm{Fc\overset{+}{C}RR'}$) are generated quantitatively when the corresponding alcohols (FcCRR′OH) are dissolved in CF_3CO_2H and give characteristic, readily interpretable ^{1}H NMR spectra in this solvent[1]. By monitoring changes with time in the spectrum, we have found that the secondary carbonium ion (I), generated from the alcohol[2] $\mathrm{FcCH(OH)CMe_3}$, rearranges cleanly and quantitatively (ca. 2 h at 70°) to the isomeric tertiary carbonium ion (II). For comparison, the latter cation was independently prepared from the alcohol[2] $\mathrm{FcCMe(OH)CHMe_2}$ in CF_3CO_2H. Signals attributable to intermediates in the rearrangement process were not detected.



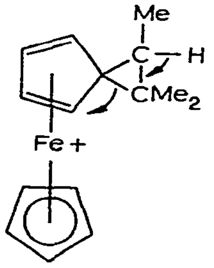
$$\mathrm{Fc{-}\overset{H}{\underset{CMe_3}{C}}{+}} \longrightarrow \mathrm{Fc{-}\overset{Me}{\underset{CHMe_2}{C}}{+}}$$

(I) (II)



$$\mathrm{Fc{-}\overset{H}{\underset{Me}{C}}{-}\overset{+}{C}Me_2}$$

(III)



(IV)

The driving force for the rearrangement (I)→(II) can be attributed to the greater thermodynamic stability of the tertiary cation[3]. Although the mechanism of the process could involve sequential methyl and hydrogen shifts*, the β-ferrocenylalkyl cation inter-

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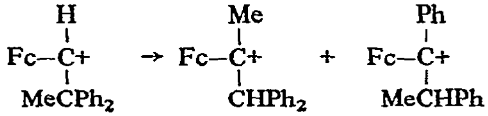
*Study of the rearrangement in CF_3CO_2D has established that the hydrogen shift occurs by an intra-ionic mechanism; H/D exchange of the migrating hydrogen atom was not observed.

mediate (III) would be thermodynamically much less stable[4] than the α-ferrocenylalkyl precursor (I). Perhaps more plausibly, the initial methyl migration may proceed synchronously with formation of a short-lived *spiro*-diene intermediate (IV) whose three-membered ring may reopen with concomitant hydrogen migration to generate the observed product (II) as indicated. *Spiro*-cyclic cations such as (IV) may be regarded as the ferrocene analogues of phenonium ions and the stereochemical course of the rearrangement sequence (I)→(IV)→(II) may be subject to orbital-symmetry control. We plan to investigate this possibility using an optically active form[5] of the precursor (I).



$$\mathrm{Fc{-}\overset{H}{\underset{MeCPh_2}{C}}{+}} \rightarrow \mathrm{Fc{-}\overset{Me}{\underset{CHPh_2}{C}}{+}} + \mathrm{Fc{-}\overset{Ph}{\underset{MeCHPh}{C}}{+}}$$

(V) (VI) (VII)

We have observed similar double-shift rearrangements of other secondary ferrocenylcarbonium ions[*]. For example, the cation (V) rearranges readily in CF_3CO_2H giving a mixture of isomeric tertiary cations. The major product (VI) results from interchange of methyl and hydrogen. The minor product (VII), resulting from phenyl/hydrogen interchange, exists in diastereoisomeric forms (the $\mathrm{Fc\overset{+}{C}RR'}$ system is itself chiral[5]) and we have independently shown that these diastereoisomers (each a racemate) interconvert in solution by rotation around the bond exocyclic to the ferrocenyl group. We have found, however, that other secondary cations (*e.g.* $\mathrm{Fc\overset{+}{C}HCHMe_2}$ and $\mathrm{Fc\overset{+}{C}HCH_2CMe_3}$) are unchanged after several hours at 70° in CF_3CO_2H.

REFERENCES

1 *Cf.*, T.D. Turbitt and W.E. Watts, *J. Chem. Soc. Chem. Commun.*, (1972) 947
2 F.H. Hon and T.T. Tidwell, *J. Org. Chem.*, 37 (1972) 1782
3 E.A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, 91 (1969) 509
4 *Cf.*, M.J. Nugent, R.E. Carter and J.H. Richards, *J. Amer. Chem. Soc.*, 91 (1969) 6145
5 *Cf.*, T.D. Turbitt and W.E. Watts, *J. Chem. Soc. Chem. Commun.*, (1973) 182

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[*] Some rearrangements reported by Hon and Tidwell[2] may proceed by a similar carbonium ion mechanism.