Stable Carbocations. Part X.[1] Generation, Observation, and Reactions of Ferrocenyl-stabilised Cyclopropylalkylium and Related Ions

By **William E. Watts,** School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland

In trifluoroacetic acid solutions, 1-ferrocenyl-1-cyclopropylalkylium ions are stable and show no tendency towards rearrangement. When these solutions are quenched with aqueous sodium carbonate, mixtures of products are formed including those of cyclopropyl ring opening. In the same acid solvent, 4-ferrocenylbut-3-en-1-ols undergo protonation giving 1-ferrocenyl-4-hydroxyalkylium ions which are slowly converted into their *O*-trifluoroacetyl derivatives. On deprotonation, the former ions give 2-ferrocenyltetrahydrofurans; the latter afford mainly the trifluoroacetates of the starting ferrocenylbutenols. Hydrolysis of these esters in acetate-buffered aqueous acetone gives alcohols without rearrangement.

In an earlier paper,[2] we described a study of the properties of stable 1-ferrocenylallylium ions. As an extension of this work, we considered the possibility that generation and observation of ferrocenyl-stabilised homoallylic cations of the type (1) might be practicable. In principle, such alkylium ions [3] may be represented as a resonance hybrid of cyclopropylmethylium (2), but-3-enylium (3), and cyclobutylium (4) species and one can envisage their generation through ionisation of appropriate precursors structurally related to one or other of these canonical forms. In view of the availability of suitable starting materials, we chose to attempt the preparation of cations formally of the types (2) and (3), to investigate their structures by ${}^1H$ n.m.r. spectroscopy, and to identify their products of collapse.

Synthetic Methods.—A series of 1-cyclopropyl-1-ferrocenylalkanols (6a—c) was obtained by reactions of the known [4] ketone (5) with lithium aluminium hydride,

methyl-lithium, and phenyl-lithium, respectively. Related homoallylic alcohols were prepared by the route

(1)   (2)   (3)   (4)

(5)   (6)

a; R = H
b; R = Me
c; R = Ph
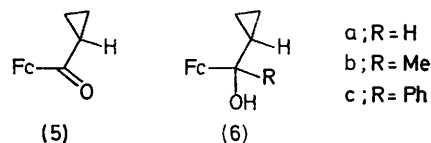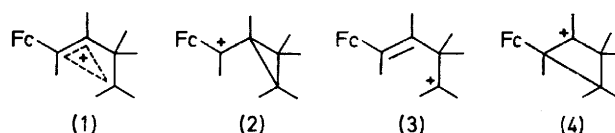
shown in Scheme 1. Reduction of the readily available [5] oxo-ester (7) with borohydride gave the lactone [6] (8)

[1] Part IX, T. S. Abram and W. E. Watts, *J.C.S. Perkin I,* 1975, 116.

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

[3] P. R. Story and B. C. Clark, 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley–Interscience, New York, 1972, vol. III, ch. 23; K. B. Wiberg, B. A. Hess, and A. J. Ashe, *ibid.,* ch. 26.
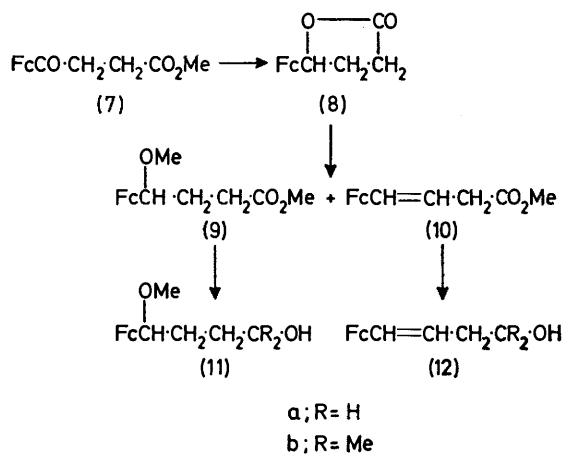
[4] W. M. Horspool, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc. (C),* 1971, 1558.

[5] K. L. Rinehart, R. J. Curby, and P. E. Sokol, *J. Amer. Chem. Soc.,* 1957, **79,** 3420; A. N. Nesmeyanov, N. A. Vol'kenau, and V. D. Vil'chevskaya, *Doklady Akad. Nauk S.S.S.R.,* 1958, **118,** 512.

[6] J. W. Huffman and D. J. Rabb, *J. Org. Chem.,* 1961, **26,** 3588.

[7] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II,* 1974, 177.

which, on treatment with acidified methanol, was converted into a chromatographically separable mixture of the saturated (9) and unsaturated (10) esters. Reactions of these esters with lithium aluminium hydride and with methyl-lithium gave the corresponding alcohols (11a and b) and (12a and b). The magnitudes of the vinylic

$$FcCO \cdot CH_2 \cdot CH_2 \cdot CO_2Me \longrightarrow Fc\overset{|}{C}H \cdot CH_2 \cdot CH_2$$
$$(7) \qquad\qquad (8)$$

$$Fc\overset{OMe}{\overset{|}{C}}H \cdot CH_2 \cdot CH_2 CO_2Me + FcCH{=}CH \cdot CH_2 \cdot CO_2Me$$
$$(9) \qquad\qquad\qquad (10)$$

$$Fc\overset{OMe}{\overset{|}{C}}H \cdot CH_2 \cdot CH_2 \cdot CR_2 \cdot OH \qquad FcCH{=}CH \cdot CH_2 \cdot CR_2 \cdot OH$$
$$(11) \qquad\qquad\qquad (12)$$

a; R = H
b; R = Me

SCHEME 1

coupling constants (ca. 16 Hz) from the ^{1}H n.m.r. spectra of the ester (10) and the derived alcohols (12a and b) established for each compound a *trans*-substituted double bond.

with time although slow deterioration in the quality of the spectrum of the secondary species (13a) was evident, due to the gradual formation of paramagnetic ferricenium or decomposition material.

(13)   (14)

a; R = H
b; R = Me
c; R = Ph

(15)   (16)
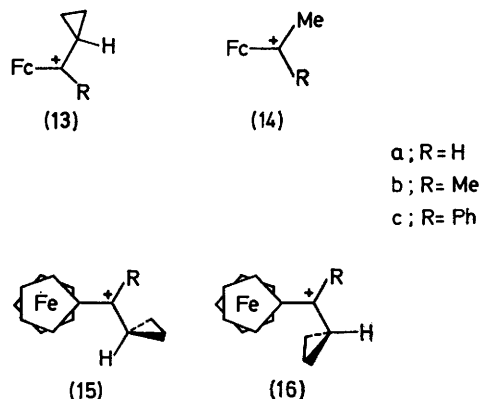
We have previously shown [7] that there exists an appreciable energy barrier to rotation around the Fc–C$^+$ bond in ferrocenylalkylium ions (E_a values in the range 70—90 kJ mol^{-1}) and it is well established [8] that cyclopropylalkylium ions favour a 'bisected' geometry to maximise charge delocalisation by the cyclopropyl group. With these factors in mind, two preferred conformations, (15) and (16), of 1-ferrocenylcyclopropylalkylium ions would be expected. Evaluation of their chemical

TABLE 1

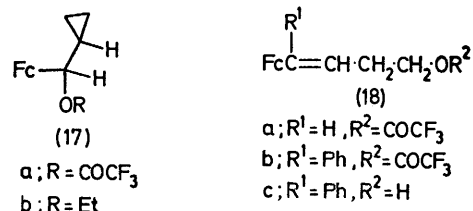^{1}H N.m.r. spectra of ferrocenylalkylium ions (13) and (14) [a]

	Ferrocenyl protons (τ) [b]			Other protons (τ) [b]		
Cation	H-2, -5	H-3, -4	H-1' to -5'	Cyclopropyl	R	Me
(13)	4.65—4.85, 5.45—5.65	3.55—3.75, 3.8—4.0	4.95 (s)	8.1—9.3	3.05br (d)	
(13b) [c]	4.5—4.65, 4.8—4.95	3.5—3.8	5.10 (s)	7.6—8.8	8.15 (s)	
(13c)	4.4—4.55, 5.4—5.6	3.5—3.7, 3.7—3.9	5.12 (s)	7.6—9.2	2.2—2.8	
(14a) [d]	4.9—5.05, 5.45—5.55	3.55—3.7, 3.7—3.85	4.97 (s)		2.88 (q)	7.75 (d)
(14b) [d]	5.05 (t)	3.72 (t)	5.14 (s)		7.77 (s)	7.77 (s)
(14c) [d]	4.6—4.75, 5.0—5.15	3.5—3.8	5.17 (s)		2.0—2.6	7.60 (s)

[a] Solvent CF$_3$·CO$_2$H with Me$_4$Si as internal reference. [b] Integrated relative intensities of signals agreed with the proton assignments; multiplets unless indicated otherwise. [c] Solutions of the alcohol (6b) and the alkene (19) in CF$_3$·CO$_2$H gave identical spectra. [d] Generated from the corresponding alcohols.

Properties of Cyclopropylalkylium Ions.—The alcohols (6a—c) dissolved readily in strong protic acids giving deeply coloured solutions containing the corresponding alkylium ions (13a—c). The ^{1}H n.m.r. spectra of these cations (solvent CF$_3$·CO$_2$H) are summarised in Table 1, in which the resonances of the methyl (for cyclopropyl) analogues (14a—c) are included for comparison. The cyclopentadienyl proton-resonance patterns in the spectra of the cations (13) are similar to those for the model systems, indicating substantial delocalisation of charge by the ferrocenyl group. These spectra, which are obviously incompatible with homoallylic charge-delocalised structures of the type (1),* were unchanged

shifts (Table 1) and comparison with those of the methyl analogues (14) suggests strongly that the cations (13a)

(17)

a; R = COCF$_3$
b; R = Et

$$Fc\overset{R^1}{\overset{|}{C}}{=}CH \cdot CH_2 \cdot CH_2 \cdot OR^2$$
(18)

a; R^1 = H, R^2 = COCF$_3$
b; R^1 = Ph, R^2 = COCF$_3$
c; R^1 = Ph, R^2 = H

and (13b) favour the sterically less-crowded conformation (15a and b), since the abnormal shielding of the R group protons points to their time-averaged location principally

* A series of 1-alkyl- and 1-aryl-cyclopropylmethylium ions has been prepared [8a] and found to be unstable above −25 °C. Comparison of the ^{1}H n.m.r. spectra of these cations with those of the ferrocenyl-stabilised species (13) shows that charge delocalisation to the cyclopropyl ring is strongly attenuated by the ferrocenyl group.

[8] (a) C. U. Pittmann and G. A. Olah, *J. Amer. Chem. Soc.*, 1965, **87**, 5123; (b) P. von R. Schleyer and V. Buss, *ibid.*, 1969, **91**, 5880; (c) W. C. Danen, *ibid.*, 1972, **94**, 4835 and references cited therein.

in the shielding zone [9] above the cyclopropyl ring. The spectrum of the cation (13c), on the other hand, shows an abnormally shielded H-2 of the cyclopentadienyl ring, in accord with a substantial population of the alternative conformation (16c).*

Solutions of the cations (13a—c) in $CF_3 \cdot CO_2H$ were quenched with a large excess of saturated aqueous sodium carbonate and the product mixtures were separated by column (Al_2O_3) and/or thin-layer (SiO_2) chromatography. The product thereby obtained from the secondary alkylium ion (13a) consisted mainly (>90%) of the highly reactive trifluoroacetate (17a)

amounts of this alcohol and the starting alcohol (6c) were also isolated from the quenching reaction.

A complex mixture of products resulted from quenching the tertiary alkylium ion (13b), and the i.r. spectrum of the mixture showed the presence of trifluoroacetate (characteristic [11] carbonyl stretching absorption around 1 790 cm^{-1}). In order to facilitate separation of this mixture, it was convenient to convert the trifluoroacetates present into the corresponding alcohols by reduction with lithium aluminium hydride. Chromatographic separation of this reduced product gave the alkenes (19) [4] and (24), the ferrocenophanes (25) and (26),
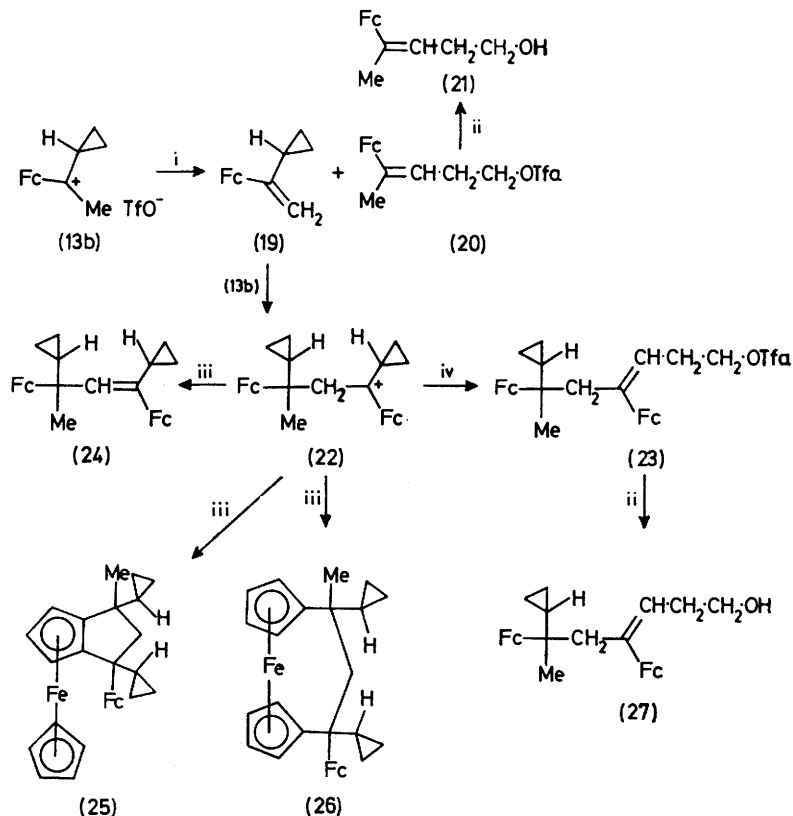
SCHEME 2   i, aq. Na_2CO_3; ii, LiAlH$_4$–Et$_2$O; iii, $-H^+$; iv, TfaO$^-$ Tfa = $CF_3 \cdot CO$

which, on treatment with ethanol, underwent rapid conversion into the ether (17b). Minor amounts of the ring-opened ester (18a) were also formed in the quenching experiment. This product was identified by reduction with lithium aluminium hydride, which afforded the *trans*-alkenol (12a), identical with the product previously prepared. At the other extreme of reactivity, the phenyl-substituted cation (13c) on quenching gave mainly (>80%) the ring-opened product (18b), which underwent quantitative reduction by lithium aluminium hydride to the corresponding alcohol (18c). Minor

and the alcohols (21) and (27). These alcohols almost certainly result from reduction of the esters (20) and (23) formed in the original reaction. The mode of formation of these products is suggested in Scheme 2. Initially, the cation (13b) collapses both by cyclopropyl ring-opening with trifluoroacetate capture to give (20) (*ca.* 33%) and by deprotonation to give (19). Unconsumed cation (13b) then adds to the latter alkene, generating the new alkylium ion (22), which leads to products of ring-opening (23), deprotonation (24), and internal electrophilic substitution [(25) and (26)]. The formation of the products (24)—(26) was not unexpected; a range of

* The spatial requirements of the ferrocenyl and phenyl groups are similar in magnitude.[10]

[9] See L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, New York, 1969, p. 98.

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

[11] See L. J. Bellamy, ' The Infra-red Spectra of Complex Molecules,' Methuen, London, 1958, p. 183.

structurally similar compounds results on quenching the 1-ferrocenyl-1-methylethylium ion (14b).[12]

These results show that the propensity towards formation of cyclopropyl ring-opened products increases markedly through the series: (13a) < (13b) < (13c).* Although steric factors may contribute towards this variation in reactivity, electronic effects are likely to be of predominant importance. Recent [13]C n.m.r. studies [14] have established that the concentration of positive

hand, the spectra of the ester (18b) and the derived alcohol (18c), both liquid, contained two C_5H_5 singlets of unequal intensity. Although separation was not achieved, it seems likely that these products consist of mixtures of E- and Z-stereoisomers resulting from reaction of the cation in both conformations (15c) and (16c).

Cations derived from Homoallylic Alcohols.—The alcohols (12a), (12b), (18c), (21), and (27) dissolved

TABLE 2

¹H N.m.r. spectra of ferrocenylalkylium ions (28) and (29) [a]

Cation	Ferrocenyl protons (τ) [b]			Other protons (τ) [b,e]	
	H-2, -5	H-3, -4	H-1'—5'	R¹	R²
(28a)	4.9—5.1, 5.4—5.6	3.6—3.9	4.95 (s)	2.9—3.2	6.04br (t)
(28b)	4.85—5.05, 5.4—5.6	3.6—3.9	4.92 (s)	2.8—3.15	8.56 (s)
(28c)	4.8—5.0	3.5—3.65	4.98 (s)	7.68 (s)	5.94br (t)
(28d)	4.8—5.0, 5.1—5.3	3.5—3.65	5.15 (s)	2.2—2.7	6.18br (t)
(29a)	4.9—5.1, 5.4—5.6	3.6—3.9	4.98 (s)	2.9—3.2	5.52br (t)
(29b)	4.8—5.0, 5.4—5.6	3.6—3.9	4.98 (s)	2.8—3.2	8.32 (s)
(29c)	4.95—5.15	3.55—3.75	5.08 (s)	7.72 (s)	5.48br (t)
(28d)	4.75—4.95, 5.1—5.3	3.55—3.8	5.18 (s)	2.2—2.7	5.70br (t)

[a,b] As for Table 1.   [e] The $^+C \cdot CH_2 \cdot CH_2$ resonances appear as an ill-defined complex multiplet in the range τ 7.0—8.5.   The OH resonance of the cations (28a—d) was not observed (fast exchange with solvent).

charge at the C^+ atom of ferrocenylalkylium ions increases with alkyl and more particularly with phenyl substitution at this carbon, i.e. $Fc\overset{+}{C}H_2$ < $Fc\overset{+}{C}HMe$ < $Fc\overset{+}{C}Me_2$, and $Fc\overset{+}{C}HMe$ < $Fc\overset{+}{C}HPh$. Assuming this effect to be present for the cations (13), the demand for electron donation from the cyclopropyl group, which would be associated with a weakening of the ring C–C bonds, would be greatest for the phenyl-substituted species (13c) and least for the secondary alkylium ion (13a). Accordingly, the former undergoes ring opening much more readily than the latter, for which such reaction occurs only to a very minor extent.

The stereochemistry of the product of ring opening of a cation of the type (13) would be determined by the conformation(s), (15) or (16), of the species at the moment of reaction.[15,†] The apparently exclusive formation of the *trans*-alkene (18a) from the cation (13a) suggests that the conformation (15a) is favoured, in agreement with the conclusion reached previously (¹H n.m.r.). From the sharp m.p. of the alcohol (21) obtained from the product (20) of reaction of the cation (13b) and from the clearly defined ¹H n.m.r. spectra of this compound (see Experimental section), it appears that ring opening occurs stereospecifically, probably (see before) by collapse of the conformer (15b). On the other

readily in $CF_3 \cdot CO_2H$. The ¹H n.m.r. spectra of these solutions (see Table 2) showed clearly that protonation of the double bond had occurred to give the corresponding ferrocenylalkylium ions (28a—e). There was no evidence for the presence of cations of the types (1) or (2) whose formation by acid-promoted hydroxide removal with ferrocenylvinyl participation might have been anticipated. The cations (28a and b) were also obtained from the ether alcohols (11a and b, respectively) by elimination of methanol in $CF_3 \cdot CO_2H$. These 4-hydroxy-alkylium ions undergo slow esterification in $CF_3 \cdot CO_2H$ with formation of the corresponding trifluoroacetate cations (29). In the case of the primary alcohols (28a, c, and d), this reaction is conveniently monitored by observing the disappearance in the ¹H n.m.r. spectra of the $CH_2 \cdot OH$ multiplet and its replacement at lower field by the corresponding $CH_2 \cdot O \cdot CO \cdot CF_3$ resonance.

When solutions of the cations (28a and b) in $CF_3 \cdot CO_2H$ were quenched with aqueous carbonate immediately after their preparation, the tetrahydrofurans (30a and b, respectively) were formed by intramolecular hydroxy capture. These cyclic ethers underwent ring opening in $CF_3 \cdot CO_2H$, regenerating the precursors (28a and b). Solutions of the alcohols (21) and (18c) in $CF_3 \cdot CO_2H$ were set aside until formation of the ester cations (29c and d respectively) was complete. When these solutions were quenched as before, the esters (20) and (18b) respectively

* Indirect evidence has recently been obtained to suggest that the cations (13a and b) are resistant to ring opening, which does occur, however, when two geminal methyl substituents are attached to the cyclopropyl ring.[13]

† The preference of 1-cyclopropylalkylium ions for a ' bisected ' conformation is strongly attenuated with decrease in positive charge at the C^+ atom.[8e]

[12] W. M. Horspool, R. G. Sutherland, and J. R. Sutton, *Canad. J. Chem.*, 1970, **48**, 3542; W. M. Horspool, P. Stanley, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc. (C)*, 1971, 1365; W. M. Horspool, R. G. Sutherland, and B. J. Thomson, *Synthesis in Inorg. and Metal-Org. Chem.*, 1972, **2**, 129.
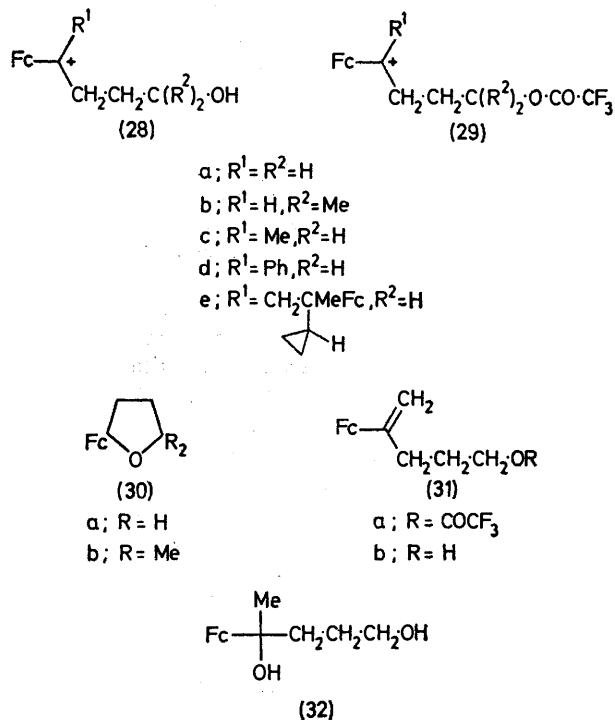
[13] W. M. Horspool and B. J. Thomson, *Tetrahedron Letters*, 1974, 3529.

[14] G. H. Williams, D. D. Traficante, and D. Seyferth, *J. Organometallic Chem.*, 1973, **60**, C53; S. Braun and W. E. Watts, *ibid.*, 1975, **87**, C33; S. Braun, T. S. Abram, and W. E. Watts, *ibid.*, 1975, **97**, 429.

[15] S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 2882; C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, 1970, **92**, 4274; C. D. Poulter and S. Winstein, *ibid.*, 1970, **92**, 4282.

were formed as the main products. Other minor products were also detected. The terminal alkene (31a) was found (^{1}H n.m.r.) to be present in the product of deprotonation of the cation (29c). The diol (32) was also isolated as a very minor component of the mixture, containing mainly (21) and (31b), obtained by reduction (with LiAlH$_4$) of the total product of quenching the same cation. In CF$_3$·CO$_2$H solution, this diol was reconverted into the cation (28c) while the esters [(20) + (31a)] and (18b) similarly afforded the cations (29c and d respectively).

Solvolysis of the homoallylic esters (20) and (18b) in aqueous acetone buffered with sodium acetate gave

(28) (29)

a; R^1 = R^2 = H
b; R^1 = H, R^2 = Me
c; R^1 = Me, R^2 = H
d; R^1 = Ph, R^2 = H
e; R^1 = CH$_2$CMeFc, R^2 = H

(30) (31)

a; R = H   a; R = COCF$_3$
b; R = Me   b; R = H

(32)

exclusively the alcohols (21) and (18c), respectively, without rearrangement. No trace of the products of S_N1 reaction with ferrocenylvinyl participation [i.e. (6b and c)] was detected.

Fragmentation Reactions.—The alkene (24) and the ferrocenophanes (25) and (26) each dissolved in CF$_3$·CO$_2$H giving the cation (13b) as the only detected (^{1}H n.m.r.) product. We have previously encountered similar behaviour with structurally related compounds and have proposed a mechanism for the fragmentation.[16] The alcohol (27) reacts in an analogous fashion, affording an equimolar mixture of the cations (13b) and (29c) after a few hours in CF$_3$·CO$_2$H at 33 °C, by fragmentation of the intermediate cation (29e).

EXPERIMENTAL

For general details, see Part IV.[7]

1-*Ferrocenylcyclopropylmethanol* (6a).—This alcohol,[13] a viscous yellow oil, was prepared in quantitative yield by reduction of the ketone [4] (5) with LiAlH$_4$ in ether and was

purified by chromatography [Al$_2$O$_3$; light petroleum–ether (2 : 1)] (Found: C, 66.1; H, 6.3. C$_{14}$H$_{16}$FeO requires C, 65.7; H, 6.3%); τ 5.6—5.9 (4 H, m, C$_5$H$_4$), 5.80 (5 H, s, C$_5$H$_5$), 6.2br (1 H, d, C*H*·OH), 7.89br (1 H, s, OH), and 8.6—9.8 (5 H, m, cyclopropyl). This alcohol is unstable when adsorbed on SiO$_2$.

1-*Ferrocenyl-1-phenylcyclopropylmethanol* (6c).—This alcohol, a bright yellow solid, m.p. (from light petroleum) 70—71°, was prepared by the addition of PhLi to the ketone [4] (5) in ether–benzene (quantitative yield) and was purified by chromatography [Al$_2$O$_3$; light petroleum–ether (2 : 1)] (Found: C, 72.0; H, 6.0. C$_{20}$H$_{20}$FeO requires C, 72.3; H, 6.1%); τ 2.5—2.85 (5 H, m, Ph), 5.35—5.5 and 5.9—6.05 (4 H, 2m, C$_5$H$_4$), 5.86 (5 H, s, C$_5$H$_5$), 7.42 (1 H, s, OH), and 8.3—9.8 (5 H, m, cyclopropyl).

5-*Ferrocenyltetrahydrofuran-2-one* (8).—NaBH$_4$ (3.0 g) was added to a solution of the ester [5] (7) (8.1 g, 27 mmol) in methanol (100 ml) and the mixture was refluxed with stirring for 2 h. The solution was then diluted with water (500 ml) and extracted with ether. The extract was washed (H$_2$O), dried (MgSO$_4$), and evaporated, giving the lactone (8) (6.6 g, 90%), a yellow solid, m.p. (from light petroleum–ether) 133—134° (lit.,[6] 132—133°); τ 4.63 (1 H, t, CH), 5.76 and 5.79 (9 H, 2s, Fc), and 7.2—7.8 (4 H, m, CH$_2$CH$_2$).

Preparation of the Esters (9) *and* (10).—A solution of the lactone (8) (5.4 g, 20 mmol) in methanol (200 ml) containing concentrated hydrochloric acid (5 ml) was refluxed for 4 h, then diluted with water (500 ml), and extracted with ether. The extract was washed (aqueous Na$_2$CO$_3$ then H$_2$O), dried (MgSO$_4$), and evaporated, and the residual orange liquid was dissolved in light petroleum and chromatographed on Al$_2$O$_3$ (deactivated by exposure to the atmosphere for 24 h). Light petroleum–ether (50 : 1) eluted *methyl trans-4-ferrocenylbut-3-enoate* (10) (2.9 g, 50%), a dark orange solid, m.p. (from light petroleum) 35—36° (Found: C, 63.5; H, 5.7. C$_{15}$H$_{16}$FeO$_2$ requires C, 63.4; H, 5.7%); τ 3.6—4.4 (2 H, AB portion of ABX$_2$, vinyl, J_{AB} 15.5 Hz), 5.69 and 5.84 (4 H, 2t, C$_5$H$_4$), 5.92 (5 H, s, C$_5$H$_5$), 6.34 (3 H, s, OMe), and 6.94 (2 H, d, CH$_2$). Light petroleum–ether (20 : 1) eluted *methyl 4-ferrocenyl-4-methoxybutanoate* (9) (1.2 g, 19%), a yellow solid, m.p. (from light petroleum) 48—49° (Found: C, 61.2; H, 6.6. C$_{16}$H$_{20}$FeO$_3$ requires C, 60.8; H, 6.4%); τ 5.86br (9 H, s, Fc), 5.9—6.1 (1 H, m, CH), 6.34 (3 H, s, CO$_2$Me), 6.79 (3 H, s, CHO*Me*), and 7.4—8.0 (4 H, m, CH$_2$·CH$_2$).

4-*Ferrocenyl-4-methoxybutan-1-ol* (11a).—This alcohol, a yellow oil, was obtained in 95% yield by reduction of the ester (9) with LiAlH$_4$ in ether (Found: C, 62.7; H, 7.1. C$_{15}$H$_{20}$FeO$_2$ requires C, 62.5; H, 7.0%); ν$_{max.}$ (film) 3 380 cm^{-1} (OH); τ 5.85 (9 H, s, Fc), 5.98br (1 H, t, CH), 6.35br (2 H, t, C*H*$_2$·OH), 6.74 (3 H, s, OMe), 6.92 (1 H, s, OH), and 7.8—8.6 (4 H, m, CH$_2$CH$_2$).

5-*Ferrocenyl-5-methoxy-2-methylpentan-2-ol* (11b).—This alcohol, a yellow oil, was obtained in 88% yield by addition of MeLi to the ester (9) in ether (Found: C, 64.9; H, 7.8. C$_{17}$H$_{24}$FeO$_2$ requires C, 64.6; H, 7.7%); ν$_{max.}$ (film) 3 400 cm^{-1} (OH); τ 5.89 (9 H, s, Fc), 5.9—6.1 (1 H, m, CH), 6.75 (3 H, s, OMe), 7.40 (1 H, s, OH), 7.8—8.6 (4 H, m, CH$_2$·CH$_2$), and 8.80 (6 H, s, Me$_2$).

4-*Ferrocenylbut-3-en-1-ol* (12a).—This alcohol, obtained as orange leaflets, m.p. (from light petroleum–ether) 42—43°, was prepared in 94% yield by reduction of the ester (10) with LiAlH$_4$ in ether (Found: C, 65.8; H, 6.3. C$_{14}$H$_{16}$FeO

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requires C, 65.7; H, 6.3%); τ 3.5—4.5 (2 H, AB portion of ABX$_2$, vinyl, J_{AB} 15.5 Hz), 5.66 and 5.80 (4 H, 2t, C$_5$H$_4$), 5.89 (5 H, s, C$_5$H$_5$), 6.32 (2 H, t, CH_2·OH), 7.45—7.85 (2 H, m, allylic CH$_2$), and 8.12 (1 H, s, OH).

5-Ferrocenyl-2-methylpent-4-en-2-ol (12b).—This alcohol,[13] an orange solid, m.p. (from light petroleum–ether) 81—83°, was obtained in 87% yield by the addition of MeLi to the ester (10) in ether (Found: C, 67.7; H, 7.3. C$_{16}$H$_{20}$FeO requires C, 67.6; H, 7.1%); τ 3.7—4.5 (2 H, AB portion of ABX$_2$, vinyl, J_{AB} 16.0 Hz), 5.72 and 5.88 (4 H, 2t, C$_5$H$_4$), 5.96 (5 H, s, C$_5$H$_5$), 7.83 (2 H, d, CH$_2$), 7.85 (1 H, s, OH), and 8.81 (6 H, s, Me$_2$).

Generation and Quenching of 1-*Ferrocenylcyclopropylmethylium Ion* (13a).—The alcohol (6a) (770 mg, 3.0 mmol) was dissolved in CF$_3$·CO$_2$H (5 ml) giving a deep maroon solution containing the cation (13a); the [1]H n.m.r. spectrum was recorded immediately (see Table 1). The solution was then diluted with a large excess of saturated aqueous sodium carbonate and the organic products were extracted with ether. The extract was quickly washed (H$_2$O), dried (MgSO$_4$), and evaporated. The residual orange liquid was separated by t.l.c. (SiO$_2$; light petroleum and light petroleum–ether), giving the following products (in order of increasing polarity): the ester (17a) (960 mg, 91%), an extremely reactive orange-yellow liquid, $ν_{max.}$ (film) 1 795 cm^{-1} (CO), τ 5.7—6.1 (10 H, m + s, Fc + CH), and 8.5—9.8 (5 H, m, cyclopropyl); the ester (18a) (21 mg, 2%), an orange oil, $ν_{max.}$ (film) 1 790 cm^{-1} (CO); and the alcohol (6a) (23 mg, 3%).

Brief treatment of the ester (17a) with ethanol in chloroform solution gave the ether (17b) (94%), a yellow oil, which was purified by chromatography (Al$_2$O$_3$; light petroleum) (Found: C, 68.0; H, 7.2. C$_{18}$H$_{20}$FeO requires C, 67.6; H, 7.1%); τ 5.7—6.0 (10 H, m + s, Fc + CH·OEt), 6.46 (2 H, q, CH$_2$O), 8.86 (3 H, t, Me), and 8.6—9.8 (5 H, m, cyclopropyl). In CF$_3$·CO$_2$H solution, this ether gave the cation (13a) and ethanol.

Reduction of the ester (18a) with LiAlH$_4$ in ether gave a quantitative yield of the alcohol (12a), identical (i.r., [1]H n.m.r.) with the compound described previously.

Generation and Quenching of 1-*Ferrocenyl-1-methylcyclopropylmethylium Ion* (13b).—The alcohol [4] (6b) (1.08 g, 4.0 mmol) was dissolved in CF$_3$·CO$_2$H (5 ml) giving a deep maroon solution containing the cation (13b) (for [1]H n.m.r. spectrum see Table 1). The solution was then quenched with an excess of saturated aqueous sodium carbonate and the product was isolated as in the preceding experiment. The i.r. spectrum of this product contained an intense carbonyl stretching absorption at 1 795 cm^{-1} (trifluoroacetate). The total product was treated with an excess of LiAlH$_4$ in ether (to convert trifluoroacetates into alcohols) and the product thereby obtained was chromatographed [Al$_2$O$_3$; light petroleum–ether (5 : 1)]. An orange band (540 mg of product) and a more polar yellow band (524 mg of product) were eluted. These fractions were individually separated by t.l.c. (SiO$_2$). With light petroleum as solvent, the following compounds were obtained from the former fraction: the alkene [4] (19) (70 mg, 7%), an orange oil (lit.,[4] oil), τ 4.92 (1 H, d, vinyl), 5.28 (1 H, t, vinyl), 5.48 and 5.78 (4 H, 2t, C$_5$H$_4$), 5.87 (5 H, s, C$_5$H$_5$), and 8.2—9.5 (5 H, m, cyclopropyl); the *alkene* (24; mixture of *E*- and *Z*-isomers) (255 mg, 25%), an orange solid, m.p. (light petroleum) 30—33° (Found: C, 71.8; H, 6.4. C$_{30}$H$_{32}$Fe$_2$ requires C, 71.5; H, 6.4%), τ 4.85—4.95 and 5.2—5.3 (1 H, 2m, vinyl), 5.50 (2 H, t) and 5.6—5.9 (16 H, m) (Fc), 8.51 and 8.53

(3 H, 2s, Me), and 8.4—9.8 (10 H, m, cyclopropyl); and the ferrocenophanes [(25) + (26)] (125 mg, 12%), obtained as a waxy low-melting orange-yellow solid (Found: C, 71.7; H, 6.5. Calc. for C$_{30}$H$_{32}$Fe$_2$: C, 71.5; H, 6.4%); the [1]H n.m.r. spectrum of this mixture, in which the compound (26) predominated, was in accord with the composition assigned; the components could not be completely separated from each other although fractions enriched in each isomer were obtained by ' topping and tailing ' the t.l.c. band containing them.

In CF$_3$·CO$_2$H solutions, the alkenes (19) and (24) and the ferrocenophanes (25) and (26) (enriched fractions) gave identical spectra corresponding to the cation (13b).

With light petroleum–ether (9 : 1) as solvent, the following compounds were obtained from t.l.c. of the second fraction described above (in order of increasing polarity): the *alcohol* (27) (94 mg, 9%), a viscous orange-yellow oil (Found: C, 69.4; H, 6.8. C$_{30}$H$_{34}$Fe$_2$O requires C, 69.0; H, 6.6%), $ν_{max.}$ (film) 3 340 cm^{-1} (OH), τ 5.5—5.65 (1 H, m, vinyl), 5.7—6.0 (18 H, m, Fc), 6.30br (2 H, t, CH_2·OH), 7.2—8.0 (4 H, m, allylic CH$_2$), 8.50br (1 H, s, OH), 9.02 (3 H, s, Me), and 8.8—9.4 (5 H, m, cyclopropyl); and the *alcohol* (21) (356 mg, 33%), an orange-yellow solid, m.p. (from light petroleum–ether) 83—84° (Found: C, 66.8; H, 6.7. C$_{15}$H$_{18}$FeO requires C, 66.7; H, 6.7%); τ 4.15—4.6 (1 H, m, vinyl), 5.62 and 5.80 (4 H, 2t, C$_5$H$_4$), 5.88 (5 H, s, C$_5$H$_5$), 6.30 (2 H, t, CH_2·OH), 7.4—7.85 (2 H, m, allylic CH$_2$), 8.00 (1 H, s, Me), and 8.40 (1 H, s, OH).

Generation and Quenching of 1-*Ferrocenyl-1-phenylcyclopropylmethylium Ion* (13c).—The alcohol (6c) (1.00 g, 3.0 mmol) was dissolved in CF$_3$·CO$_2$H (5 ml) giving a deep purple solution containing the cation (13c) (for [1]H n.m.r. spectrum see Table 1). This solution was then quenched with aqueous sodium carbonate and the products were isolated as in the preceding experiments. A portion of this product was separated by t.l.c. (SiO$_2$; light petroleum and light petroleum–ether) giving the following products (in order of increasing polarity): the *trifluoroacetate* (18b) (81%), an orange oil (Found: C, 62.2; H, 4.7. C$_{22}$H$_{19}$F$_3$FeO$_2$ requires C, 61.7; H, 4.5%), $ν_{max.}$ (film) 1 785 cm^{-1} (CO), τ 2.5—2.9 (5 H, m, Ph), 4.11 (1 H, t, vinyl), 5.6—6.0 [11 H, m + 2 s (5.83 and 5.93), Fc + CH$_2$O], and 7.5—7.9 (2 H, m, allylic CH$_2$); the alcohol (6c) (9%), identical with the starting material; and the alcohol (18c) (5%), identical with the compound described in the following experiment.

4-Ferrocenyl-4-phenylbut-3-en-1-ol (18c).—Reduction of the ester (18b) with an excess of LiAlH$_4$ in ether and conventional work-up gave a product which was chromatographed (Al$_2$O$_3$). Light petroleum–ether (2 : 1) eluted the *alcohol* (18c) (95%), a viscous orange oil (Found: C, 72.3; H, 6.2. C$_{20}$H$_{20}$FeO requires C, 72.3; H, 6.1%); $ν_{max.}$ (film) 3 350 cm^{-1} (OH); τ 2.4—2.8 (5 H, m, Ph), 4.02 (1 H, t, vinyl), 5.84 and 5.94 (9 H, 2s, Fc), 6.40 (2 H, t, CH_2·OH), 7.6—8.1 (2 H, m, allylic CH$_2$), and 8.50br (1 H, s, OH).

Generation and Quenching of Ions derived from Homoallylic Alcohols.—Dissolution of the alcohols (12a), (12b), (18c), and (21) in CF$_3$·CO$_2$H gave solutions containing the corresponding cations (28a—d) which underwent slow esterification (several h) giving the related ester cations (29a—d). The [1]H n.m.r. spectra of these species are given in Table 2. The alcohol (27) dissolved in CF$_3$·CO$_2$H giving initially the cation (28e). When this solution was set aside for 6 h at 33 °C, fragmentation occurred giving finally a solution containing equimolar amounts of the cations (13b) and (29c).

(a) The alcohol (12a) (128 mg, 0.5 mmol) was dissolved in $CF_3\cdot CO_2H$ (3 ml) and the solution, containing the cation (28a), was immediately quenched with a large excess of saturated aqueous sodium carbonate. The product was isolated as in the preceding experiments and was separated by t.l.c. (SiO$_2$). Light petroleum eluted 2-*ferrocenyltetra-hydrofuran* (30a) (107 mg, 84%), a yellow oil (Found: C, 65.9; H, 6.3. $C_{14}H_{16}FeO$ requires C, 65.7; H, 6.3%); τ 5.1—5.4 (1 H, m, CH), 5.82 (9 H, s, Fc), 6.0—6.3 (2 H, m, CH$_2$O), and 7.6—8.2 (4 H, m, other protons). Other very minor products were not investigated. In $CF_3\cdot CO_2H$ solution, the ether (30a) was reconverted into the cation (28a).

(b) The alcohol (12b) (142 mg, 0.5 mmol) was dissolved in $CF_3\cdot CO_2H$ and the solution, containing the cation (28b), was treated as in the preceding experiment. T.l.c. separation (SiO$_2$) of the product gave 5-*ferrocenyl-2,2-dimethyltetrahydrofuran* (30b) (125 mg, 88%), a yellow solid, m.p. (from light petroleum) 49—50° (Found: C, 67.9; H, 7.2. $C_{16}H_{20}FeO$ requires C, 67.6; H, 7.1%); τ 5.05—5.35 (1 H, m, CH), 5.85 (9 H, s, Fc), 7.5—8.4 (4 H, m, CH$_2$CH$_2$), and 8.75 (6 H, s, Me$_2$).

(c) A solution of the alcohol (18c) (166 mg, 0.5 mmol) in $CF_3\cdot CO_2H$ (3 ml) was left overnight at 33 °C, giving the cation (29d). After quenching and work-up as before, separation of the product by t.l.c. (SiO$_2$) gave the ester (18b) (170 mg, 79%), identical with the product described previously, and other unidentified minor products.

(d) A solution of the alcohol (21) (270 mg, 1.0 mmol) in $CF_3\cdot CO_2H$ (5 ml) was left overnight at 33 °C, giving the cation (29c). This solution was quenched and the product was isolated as before. One half of this product was separated by t.l.c. (SiO$_2$). Light petroleum eluted an orange band which afforded a mixture of the esters (20) and (31a) (total yield 140 mg, 71%), a low-melting waxy solid; $\nu_{max.}$ (smear) 1 782 cm^{-1} (CO); τ 4.41br (t), 4.70 (m), and 5.12 (m) (vinyl protons), 5.5—5.95 (m, Fc + CH$_2$O), 7.3—8.0 (m, other CH$_2$), and 8.05 (s, Me). Integration of the vinyl signals in this spectrum gave the product ratio (20) : (31a) as *ca.* 4 : 1. Other minor products were not

investigated. The remainder of the original product mixture was dissolved in ether (50 ml) and reduced with an excess of LiAlH$_4$. The product was isolated and separated by t.l.c. (SiO$_2$) which gave two main bands. The less polar band afforded a mixture of the alcohols (21) and (31b) (total yield 103 mg, 77%). In addition to the resonances of the alcohol (21) given previously, the ^{1}H n.m.r. spectrum of this mixture contained vinyl proton signals of the isomer (31b) at τ 4.65—4.75 and 5.0—5.1. From the integration of the vinyl signals in the spectrum, the product ratio [(21) : (31b)] was *ca.* 4 : 1. Dissolution of this mixture in $CF_3\cdot CO_2H$ gave the cation (28c). The more polar band gave the diol (32) (15 mg, 9%), a viscous yellow oil; $\nu_{max.}$ (film) 3 430 cm^{-1} (OH); τ 5.75—5.95 (9 H, m + s, Fc), 6.05—6.35 (2 H, m, CH$_2$O), 7.5—8.3 (6 H, complex, other CH$_2$ + OH), and 8.45 (3 H, s, Me). Owing to the small amount of material available, elemental analysis was not carried out. In $CF_3\cdot CO_2H$ solution, this diol gave the cation (28a).

Solvolysis of the Esters (18b) *and* (20).—(a) A solution of the ester (18b) (214 mg, 0.5 mmol) in acetone (16 ml) and water (4 ml) containing sodium acetate (82 mg, 1.0 mmol) was refluxed for 10 h, then diluted with water, and extracted with ether. The extract was washed (aqueous Na$_2$CO$_3$ then H$_2$O), dried (MgSO$_4$), and evaporated. The residue (163 mg, 98%) consisted solely of the alcohol (18c), identical (i.r., ^{1}H n.m.r.) with the product described previously. No trace of the alcohol (6c) was detected.

(b) Solvolysis of the esters [(20) + (31a)] (90 mg, 0.25 mmol) in aqueous acetone containing sodium acetate was carried out as in the preceding experiment, affording a mixture of alcohols [(21) + (31b)] (60 mg, 90%), identical with the mixture obtained by reduction (LiAlH$_4$) of the same ester mixture. No trace of the alcohol (6b) was detected.