

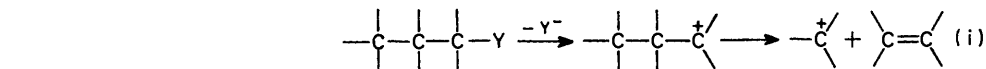
Stable Carbocations.† Part VIII.¹ Fragmentation Reactions of Ferrocenylalkylium Ions

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In solution in trifluoroacetic acid, ferrocenylalkylium ions of the type $\text{Fc}\overset{+}{\text{C}}\text{R}\cdot\text{CH}_2\text{X}$ undergo fragmentation to X^+ together with $\text{Fc}\overset{+}{\text{C}}\text{RMe}$ when X is an electrofugal group forming a sufficiently stable cation. *e.g.*, when $\text{X} = \text{FcCRMe}$ or Ph_3C but not when $\text{X} = \text{Me}_3\text{C}$ or *p*- $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$.

THE spontaneous cleavage of certain carbocations into an alkene and a structurally simpler carbocation [equation (i)] was first recognised as a possible reaction pathway by Whitmore in 1933.² Although examples of such a process have been discovered subsequently,³ these have been

limited in general to reactions of systems in which the electrofugal group is a carbocation of high thermodynamic stability (*e.g.* tropylium⁴) or to reactions in which fragmentation results in a relief of steric strain.^{3,5}



We report here an investigation of fragmentation reactions of ferrocenylalkylium ions of the type $\text{Fc}\overset{+}{\text{C}}\text{R}\cdot\text{CH}_2\text{X}$, which are readily accessible from alkene or alcohol pre-

cursors in protic acids. Previous experience has shown⁶ that the behaviour of ferrocenylalkylium ions in solution can be conveniently monitored by ¹H n.m.r. spectroscopy and we have used this technique for direct study of the fragmentation process.

We have found that cations of the type (1) fragment immediately and quantitatively in solution in trifluoroacetic acid, giving the simpler ferrocenylalkylium ions (2) and (3), the former arising by protonation of an intermediate alkene [*cf.* equation (i)]. Thus, the cation (1b) was converted into an equimolar mixture of the tertiary and secondary carbocations $\text{Fc}\overset{+}{\text{C}}\text{Me}_2$ and $\text{Fc}\overset{+}{\text{C}}\text{HMe}$, respectively, which were readily identified from their

† The series was previously entitled 'Stable Carbonium Ions'.

¹ Part VII, T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 195.

² F. C. Whitmore and E. E. Stahly, *J. Amer. Chem. Soc.*, 1933, **55**, 4153.

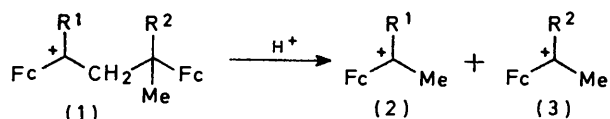
³ C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1.

⁴ K. Conrow, *J. Amer. Chem. Soc.*, 1959, **81**, 5461.

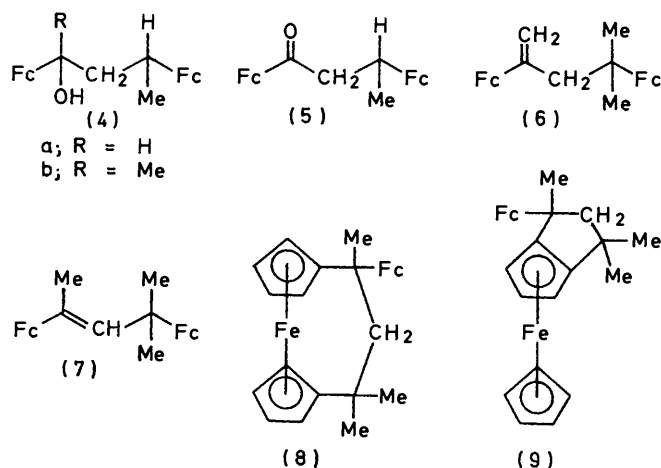
⁵ J. E. Dubois, J. S. Lomas, and D. S. Sagatys, *Tetrahedron Letters*, 1971, 1349.

⁶ T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

characteristic ^1H n.m.r. spectral patterns⁷ (see Table). Similarly, the cations (1a and c) each gave rise to a single cation ($\text{Fc}\overset{+}{\text{C}}\text{HMe}$ and $\text{Fc}\overset{+}{\text{C}}\text{Me}_2$, respectively) after



a; $\text{R}^1 = \text{R}^2 = \text{H}$
b; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$
c; $\text{R}^1 = \text{R}^2 = \text{Me}$



cleavage, fragments (2) and (3) being identical in these cases.

alcohols (4a and b), which were prepared by reactions of the ketone⁸ (5) with lithium aluminium hydride and methyl-lithium, respectively. The cation (1c), on the other hand, was formed by protonation of either of the isomeric alkenes⁹ (6) or (7). Although the ^1H n.m.r. spectra of solutions of these precursors in trifluoroacetic acid were recorded immediately following their preparation, signals attributable to the first-formed cations* (1a—c) were not observed, the spectra consisting solely of resonances characteristic of the fragmentation products (2) and (3).

We have also found that the bridged ferrocenes⁹ (8) and (9) dissolve in trifluoroacetic acid to give solutions in which the cation $\text{Fc}\overset{+}{\text{C}}\text{Me}_2$ is the only species observable (^1H n.m.r.). We have previously reported¹⁰ that diferrocenylalkanes of the type $\text{Fc}_2\text{CR}^1\text{R}^2$ undergo ready protonation and fragmentation in solution in trifluoroacetic acid [equation (ii)]. When this cleavage reaction is applied to the bridged ferrocenes (8) and (9), each is converted into the same cation (1c), whose fragmentation to the observed cation $\text{Fc}\overset{+}{\text{C}}\text{Me}_2$ has already been described. These acid-promoted transformations of the bridged ferrocenes (8) and (9) and the alkenes (6) and (7) into the cation $\text{Fc}\overset{+}{\text{C}}\text{Me}_2$, therefore, represent the reverse of the formation of these compounds from $\text{FcC}(\text{Me})=\text{CH}_2$ on treatment with a protic acid.⁹

We have also investigated the behaviour of a number of other ferrocenylalkylum systems incorporating electrofugally groups of lower thermodynamic stabilities.

^1H N.m.r. spectra (τ values) of ferrocenylalkylum ions ($\text{Fc}\overset{+}{\text{C}}\text{XY}$)^a

Cation	X	Y	Cyclopentadienyl resonances ^{b,c}			Other resonances ^b	
			α -H	β -H	1'-H	X	Y
(10)	Me	$\text{CH}_2\cdot\text{CPh}_3$	5.2—5.5	3.8—4.2	5.14(s)	8.14 (s, Me)	2.72br (s, CPh_3), 6.1—6.3 (CH_2)
(13a)	H	$\text{CH}_2\cdot\text{CH}_2\text{Ph}$	5.2—5.4, 5.5—5.65	3.6—3.8	4.96(s)	2.9—3.2 (H)	2.64br (s, Ph), 6.8—7.1 ($\text{CH}_2\cdot\text{CH}_2$)
(13b)	Me	$\text{CH}_2\cdot\text{CH}_2\text{Ph}$	5.1—5.3, 5.4—5.6	3.7—3.9	5.15(s)	7.79 (s, Me)	2.6—2.8 (Ph), 6.8—7.5 ($\text{CH}_2\cdot\text{CH}_2$)
(13c)	Me	$\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$	5.2—5.4, 5.5—5.7	3.8—4.0	5.24(s)	7.87 (s, Me)	2.8—3.3 (C_6H_4), 6.20 (s, OMe), 6.8—7.4 ($\text{CH}_2\cdot\text{CH}_2$)
(13d)	H	$\text{CH}_2\cdot\text{CMe}_3$	5.0—5.2, 5.4—5.6	3.6—3.9	4.96 (s)	2.8—3.1 (H)	7.2—8.2 (CH_2), 8.89 (s, CMe_3)
(13e)	Me	$\text{CH}_2\cdot\text{CMe}_3$	4.95—5.05, 5.1—5.2	3.6—3.8	5.15(s)	7.76 (s, Me)	7.15—7.7 (ABq, CH_2), 8.94 (s, CMe_3)
$\text{Fc}\overset{+}{\text{C}}\text{HMe}$	H	Me	4.9—5.0, 5.45—5.6	3.6—3.8	4.97 (s)	2.88 (q, H)	7.75 (d, Me)
$\text{Fc}\overset{+}{\text{C}}\text{Me}_2$	Me	Me	5.05(t)	3.72(t)	5.14(s)	7.77 (s, Me)	7.77 (s, Me)

^a Solvent $\text{CF}_3\cdot\text{CO}_2\text{H}$; Me_4Si internal reference. ^b Integrated relative intensities agreed with the proton assignments; signals were multiplets unless indicated otherwise. ^c The location of the ring protons relative to the $\overset{+}{\text{C}}\text{XY}$ substituent is indicated.

The original cations (1a and b) were generated quantitatively in trifluoroacetic acid from the corresponding

* It is conceivable that the conjugate acids (ROH_2^+) of the alcohols (4a and b) undergo concerted heterolysis and fragmentation without the intervention of the corresponding carbocations (1a and b).

⁷ Cf. M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1966, 1695; W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1967, 786.

The cation (10), for example, was readily obtained by dissolution of either of the alkenes (11) and (12) in trifluoro-

⁸ P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1962, 3880.

⁹ 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.

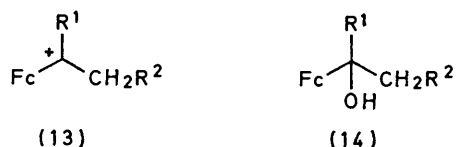
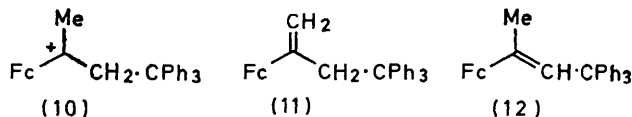
¹⁰ T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 189.

acetic acid. These isomers were synthesised by the reaction of 2-ferrocenylpropene with triphenylmethyl tetrafluoroborate in dichloromethane. The ^1H n.m.r. signals attributable to this cation (10) (see Table)

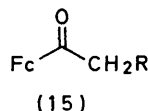


diminished with time and were gradually replaced by those of the daughter ions $\text{Fc}\overset{\oplus}{\text{C}}\text{Me}_2$ and Ph_3C^+ . At 33° , fragmentation of the ion (10) was complete after *ca.* 25 min.

The electrofugal capacities of benzyl, *p*-methoxybenzyl, and *t*-butyl groups were also investigated. The



- a; $\text{R}^1 = \text{H}, \text{R}^2 = \text{CH}_2\text{Ph}$
 b; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{CH}_2\text{Ph}$
 c; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}(p)$
 d; $\text{R}^1 = \text{H}, \text{R}^2 = \text{CMe}_3$
 e; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{CMe}_3$



- a; $\text{R} = \text{CH}_2\text{Ph}$
 b; $\text{R} = \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}(p)$
 c; $\text{R} = \text{CMe}_3$

required alcohol precursors (14a—e) were prepared from the ketones (15a—c) by reduction with lithium aluminium hydride or addition of methyl-lithium as appropriate (see Experimental section). In solution in trifluoroacetic acid, these alcohols were converted quantitatively into the corresponding carbocations (13a—e), which were found resistant to fragmentation. Even after the solutions had been heated to 55° for 2 h, no trace of the appropriate daughter ions ($\text{Fc}\overset{\oplus}{\text{C}}\text{HMe}$ or $\text{Fc}\overset{\oplus}{\text{C}}\text{Me}_2$) was detected in the ^1H n.m.r. spectra.

These results can be rationalised as follows. Carbocations of structure $\text{Fc}\overset{\oplus}{\text{C}}\text{R} \cdot \text{CH}_2\text{X}$ undergo fragmentation only in cases where an electrofugal group (X^+) of sufficient intrinsic thermodynamic stability can be expelled. The ease of the fragmentation process increases with increasing stability of the electrofugal group. Thus, under similar conditions of temperature

and concentration, cation (1b) ($\text{X}^+ = \text{Fc}\overset{\oplus}{\text{C}}\text{HMe}$; $pK_{\text{R}^+} = -0.66$)¹¹ fragments instantaneously, cation (10) ($\text{X}^+ = \text{Ph}_3\text{C}^+$; $pK_{\text{R}^+} = -6.7$)¹² fragments slowly, and cation

¹¹ E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, 1969, **91**, 509.

(13b) ($\text{X}^+ = \text{PhCH}_2^+$; $pK_{\text{R}^+} = \text{ca. } -25$)¹² remains unchanged. In cases where expulsion of X^+ does occur, the alkenylferrocene remaining undergoes immediate protonation to generate a new ferrocenylalkylium ion.

EXPERIMENTAL

For general details, see Part IV.⁶

Ferrocenyl(triphenyl)butenes (11) and (12).—Triphenylmethyl tetrafluoroborate (0.83 g, 2.5 mmol) in dichloromethane (10 ml) was added to a stirred solution of 2-ferrocenylpropene⁹ (0.56 g, 2.5 mmol) in dichloromethane (20 ml). The resulting solution was stirred for 30 s and then poured into saturated aqueous sodium hydrogen carbonate. The organic layer was separated, washed (H_2O), dried (MgSO_4), and evaporated, and the residue was separated by repeated column (Al_2O_3) and thin-layer (SiO_2) chromatography. 2-Ferrocenyl-4,4,4-triphenylbut-1-ene (11) (28 mg, 3%) was thereby obtained as yellow needles (from light petroleum-ether), m.p. $142\text{--}144^\circ$ (Found: C, 82.0; H, 5.9. $\text{C}_{32}\text{H}_{28}\text{Fe}$ requires C, 82.1; H, 6.0%), τ 2.65br (15H, s, CPh_3), 4.72 and 5.50 (1H, and 1H, 2 \times m, vinyl), 5.7—5.9 (4H, m, C_5H_4), 5.91 (5H, s, C_5H_5), and 6.0—6.2 (2H, m, CH_2). 3-Ferrocenyl-1,1,1-triphenylbut-2-ene (12) (76 mg, 8%) was similarly obtained as yellow plates (from light petroleum-ether), m.p. $145\text{--}147^\circ$ (Found: C, 82.0; H, 6.1%), τ 2.83br (15H, s, CPh_3), 3.28 (1H, m, vinyl), 5.64 and 5.84 (2H and 2H, 2 \times t, C_5H_4), 5.97 (5H, s, C_5H_5), and 8.59br (3H, s, Me). The following compounds were also isolated and were identified by comparison with authentic samples: ⁹ 2-ferrocenylpropene (103 mg, 18% recovery); the alkene (6) (8 mg, 2%); the alkene (7) (44 mg, 10%); the ferrocenophane (8) (72 mg, 16%); the ferrocenophane (9) (59 mg, 13%).

1-Ferrocenyl-3-*p*-methoxyphenylpropan-1-one (15b).—This ketone, prepared by hydrogenation of 1-ferrocenyl-3-*p*-methoxyphenylpropenone¹³ in benzene over platinum oxide, was obtained as orange prisms (from light petroleum-ether), m.p. $38\text{--}40^\circ$ (Found: C, 68.8; H, 5.6. $\text{C}_{20}\text{H}_{20}\text{FeO}$ requires C, 69.0; H, 5.8%), τ 2.7—3.3 (4H, $\text{A}_2\text{X}_2\text{q}$, C_6H_4), 5.23 and 5.53 (2H and 2H, 2 \times t, C_5H_4), 5.92 (5H, s, C_5H_5), 6.24 (3H, s, OMe), and 7.03 (4H, s, CH_2CH_2).

1-Ferrocenyl-3,3-dimethylbutan-1-one (15c).—This ketone, prepared (68%) by conventional Friedel-Crafts acylation of ferrocene in dichloromethane with 3,3-dimethylbutyryl chloride-aluminium chloride, was obtained as orange plates (from light petroleum-ether), m.p. $55\text{--}56^\circ$ (Found: C, 67.5; H, 7.0. $\text{C}_{16}\text{H}_{20}\text{FeO}$ requires C, 67.6; H, 7.1%), τ 5.20 and 5.50 (2H and 2H, 2 \times t, C_5H_4), 5.80 (5H, s, C_5H_5), 7.43 (2H, s, CH_2), and 8.93 (9H, s, CMe_3).

1-Ferrocenyl-3-phenylpropan-1-ol (14a).—This alcohol, prepared as described previously,¹³ was obtained as yellow needles (from ether), m.p. $57\text{--}59^\circ$ (lit.,¹³ $58\text{--}60^\circ$), τ 2.78 (5H, s, Ph), 5.6—5.9 (10H, m, ferrocenyl + CH), 7.0—7.4 and 7.8—8.25 (2H and 2H, 2 \times m, CH_2CH_2), and 7.96 (1H, s, OH).

1,3-Diferrocenylbutan-1-ol (4a).—This alcohol, prepared by reduction of the ketone⁸ (5) with lithium aluminium hydride, was obtained as yellow-orange needles (from ether), m.p. $105\text{--}108^\circ$ (lit.,⁸ $109\text{--}111^\circ$), τ 5.4—6.0 (18H, m,

¹² See A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York and London, 1961, p. 365.

¹³ M. J. A. Habib, J. Park, and W. E. Watts, *J. Chem. Soc. (C)*, 1970, 2556.

ferrocenyl), 6.1—6.5 (1H, m, CHOH), 7.1—7.6 (1H, m, CHMe), 8.0—8.45 (2H, m, CH₂), 8.12br (1H, s, OH), and 8.72 (3H, d, Me).

The *alcohol* (14d), similarly prepared from the ketone (15c), was obtained as yellow needles (from pentane), m.p. 46—48° (Found: C, 67.0; H, 7.5. C₁₆H₂₂FeO requires C, 67.2; H, 7.8%), τ 5.7—5.9 (10H, m, ferrocenyl + CH), 8.36br (2H, d, CH₂), 8.46 (1H, s, OH), and 9.03 (9H, s, CMe₃).

2,4-Diferrocenylpentan-2-ol (4b).—This *alcohol*, prepared by the addition of methyl-lithium to the ketone ⁸ (5) by the method described previously,⁶ was obtained as yellow plates (from ether), m.p. 104—106° (Found: C, 66.0; H, 6.3. C₂₅H₂₈Fe₂O requires C, 65.8; H, 6.2%), τ 5.81 and 5.94 (5H and 5H, 2 \times s, C₅H₅), 5.7—6.15 (8H, m, C₅H₄), 7.2—7.65 (1H, m, CH), 7.99br (1H, s, OH), 8.0—8.25 (2H, m, CH₂), 8.47 (3H, s, Me), and 8.83 (3H, d, Me).

The *alcohol* (14b), similarly prepared from the ketone ¹³ (15a), was obtained as orange prisms (from light petroleum-ether), m.p. 59—61° (Found: C, 71.8; H, 6.6. C₂₆H₂₂FeO requires C, 71.9; H, 6.6%), τ 2.85 (5H, s, Ph), 5.7—5.9 (4H,

m, C₅H₄), 5.78 (5H, s, C₅H₅), 7.2—7.5 and 7.9—8.3 (2H and 2H, 2 \times m, CH₂CH₂), 7.88br (1H, s, OH), and 8.45 (3H, s, Me).

The *alcohol* (14c), similarly prepared from the ketone (15b), was obtained as orange-yellow prisms (from light petroleum-ether), m.p. 62—64° (Found: C, 69.2; H, 6.7. C₂₁H₂₄FeO requires C, 69.2; H, 6.6%), τ 2.9—3.4 (4H, A₂X₂Q, C₆H₄), 5.7—5.9 (9H, m, ferrocenyl), 6.29 (3H, s, OMe), 7.3—7.6 and 8.0—8.3 (2H and 2H, 2 \times m, CH₂CH₂), 7.89br (1H, s, OH), and 8.46 (3H, s, Me).

The *alcohol* (14e), similarly prepared from the ketone (15c) was obtained as orange-yellow plates (from pentane), m.p. 64—66° (Found: C, 68.2; H, 8.1. C₁₇H₂₄FeO requires C, 68.0; H, 8.1%), τ 5.7—5.9 (4H, m, C₅H₄), 5.80 (5H, s, C₅H₅), 7.89 (1H, s, OH), 8.45 (2H, m, CH₂), 8.49 (3H, s, Me), and 9.13 (9H, s, CMe₃).

We thank Dr. T. D. Turbitt for various samples and the Northern Ireland Department of Education for a maintenance grant (to T. S. A.).

[4/1555 Received, 26th July, 1974]