Stable Carbocations. Part IX.[1] Reactions involving Sterically Crowded Ferrocenylalkylium Ions

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The 1-ferrocenyl-1,2,2,3,3-pentamethylbutylium ion (6) is formed when 3-ferrocenyl-2,2,4,4-tetramethylpentan-3-ol (1) is dissolved in trifluoroacetic acid. At 33°, this cation reacts both by fragmentation [to give the 1-ferrocenyl-1,2-dimethylpropylium ion (7)] and by rearrangement [to the 1,2-dimethyl-1-(2-t-butylferrocenyl)propylium ion (10)]. At 65°, the cation (10) rearranges to the 2,2-dimethyl-1-(2-t-butylferrocenyl)propylium ion (14).

As part of a study of steric crowding in organic chemistry, Hon and Tidwell investigated the behaviour of several highly substituted (1-hydroxyalkyl)ferrocenes in acidic media.[2] In particular, they reported that brief treatment of the highly crowded alcohol (1) with perchloric–acetic acid followed by aqueous sodium hydrogen carbonate led to the rearranged alkene (2) (65%) and the alcohols (3) (16%) and (4) (1%). A speculative series of carbocation rearrangements was advanced to account for the generation of these products. From our knowledge of the properties of ferrocenylalkylium ions gained in earlier studies (see Parts I—VIII), we were doubtful of several of the reaction pathways suggested by these authors, and now report the results of a reinvestigation of this reaction.

(1)   (2)   (3)   (4)
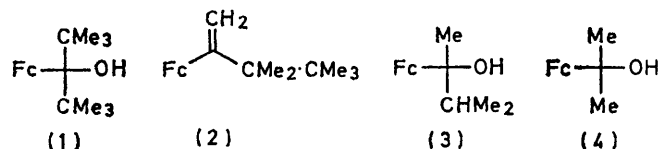
Treatment of the alcohol (1) as described previously[2] gave results similar to those reported.[2] The alkene

† The mechanism of formation of this cation from the alcohol (1) is unknown. It is not formed when the alkene (2) is dissolved in trifluoroacetic acid.

‡ It is conceivable that the conjugate acid ($R\overset{+}{O}H_2$) of the alcohol (1) may be converted *via* the spiro-diene intermediate (24) into the cation (6) without the intervention of the cation (5).

(2) and alcohol (3) were the main products, with small amounts of the alcohol (4) also present. We also found that similar product mixtures could be formed from the alcohol (1) by using trifluoroacetic acid as acidic solvent. Since the behaviour of ferrocenyl-alkylium ions in trifluoroacetic acid can be conveniently monitored by [1]H n.m.r. spectroscopy,[1,3] we used this technique to follow the progress of the reaction. In order to facilitate identification of the likely carbocations formed, the [1]H n.m.r. spectra of the cations (6), (7), and $Fc\overset{+}{C}Me_2$ were recorded by using solutions of the alkene (2) and the alcohols (3) and (4), respectively, in trifluoroacetic acid. These spectra are summarised in Table 1.

The [1]H n.m.r. spectrum of a freshly prepared solution of the alcohol (1) in trifluoroacetic acid at 33° showed clearly that the carbocation (6) was almost exclusively the cationic species initially present. Weak signals due to $Fc\overset{+}{C}Me_2$ † were the only other resonances present. Signals attributable to the ion (5) were not detected, even when the spectrum of a solution of the alcohol (1) in trifluoroacetic acid at −15° was recorded immediately following its preparation. The rearrangement of the first-formed cation ‡ (5) to the observed

[1] Part VIII, T. S. Abram and W. E. Watts, preceding paper.
[2] F. H. Hon and T. T. Tidwell, *J. Org. Chem.*, 1972, **37**, 1782.
[3] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

cation (6) must therefore occur with extreme ease, the driving force being presumably relief of steric strain in the precursor.

The cation (6) itself was found to be unstable in tri-

(10), in the relative molar proportions $ca.$ 2 : 1, respectively. The conversion of (6) into the t-butyl ester and the cation (7), which were formed in equimolar proportions, represents a fragmentation reaction

TABLE 1

^{1}H N.m.r. spectra (τ values) of unsubstituted ferrocenylalkylium ions $\overset{+}{Fc}CXY$ [a]

Cation	X	Y	Cyclopentadienyl resonances [b,c]			Other resonances [b]	
			α-H	β-H	1′-H	X	Y
(6)	Me	CMe$_2$·CMe$_3$	4·45—4·55, 4·7—4·8	3·4—3·8	5·05 (s)	8·08 (s, Me)	8·37, 8·50 (2 × s, CMe$_2$), 8·98 (s, CMe$_3$)
(7)	Me	CHMe$_2$	4·85—5·0	3·6—3·75	5·02 (s)	7·90 (s, Me)	7·0—7·5 (CH), 8·44, 8·69 (2 × d, CHMe_2)
$Fc\overset{+}{C}Me_2$	Me	Me	5·05(t)	3·72(t)	5·14(s)	7·77 (s, Me)	7·77 (s, Me)

[a] Solvent CF$_3$·CO$_2$H; Me$_4$Si 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 $\overset{+}{C}XY$ substituent is indicated.
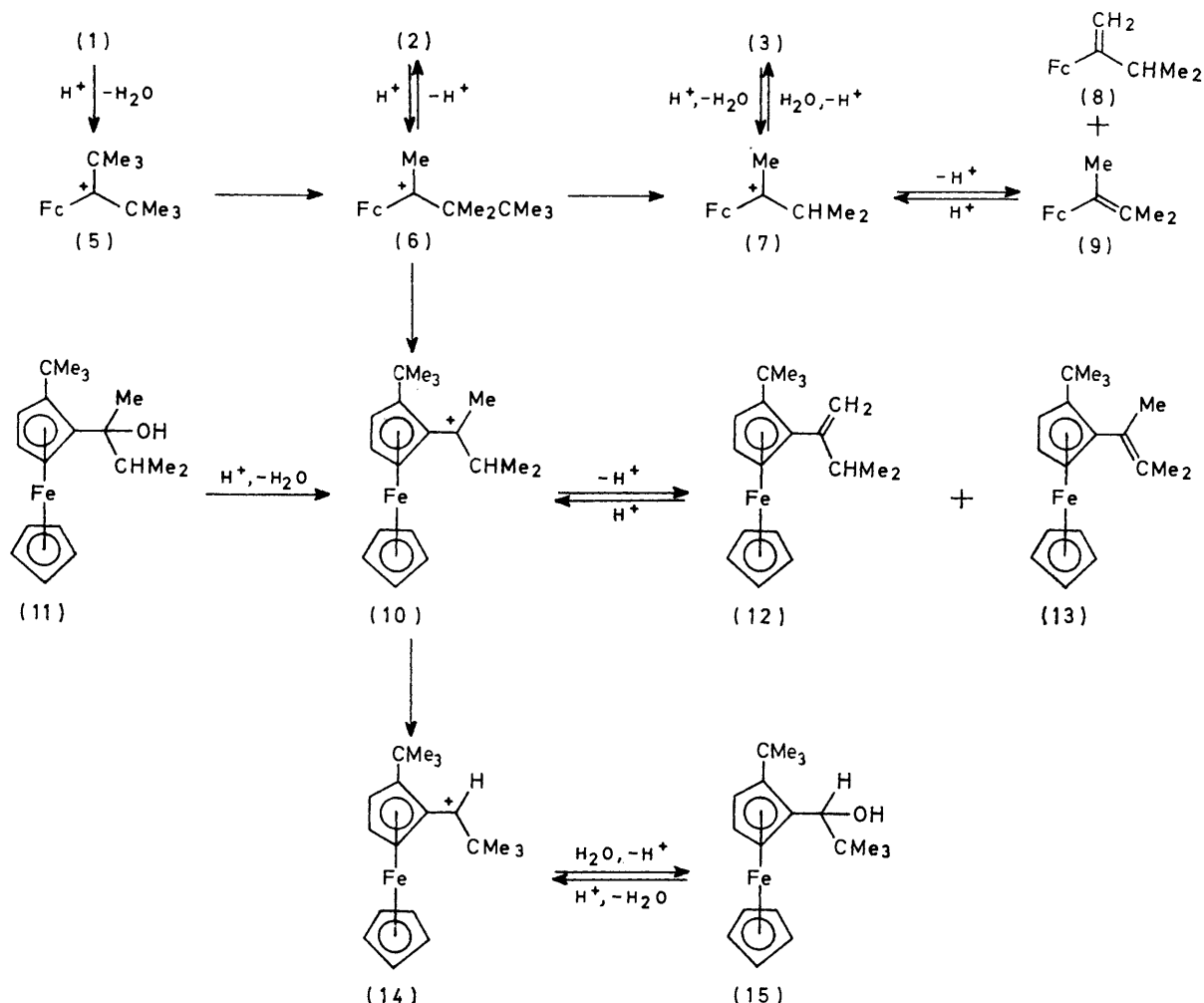
SCHEME 1

fluoroacetic acid at 33°. During $ca.$ 15 min, complete reaction occurred to give t-butyl trifluoroacetate, identified by spectral comparison with an authentic sample, and two new ferrocenylalkylium ions, (7) and

[4] J. E. Dubois, J. S. Lomas, and D. S. Sagatys, *Tetrahedron Letters*, 1971, 1349; see C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1.

of the type studied earlier.[1] We had previously found [1] that cations of the structure $Fc\overset{+}{C}R·CH_2CMe_3$ resist fragmentation under similar conditions. The driving force for the expulsion of Me$_3$C$^+$ from the cation (6) must therefore be derived from a relief of steric strain; related fragmentations of similarly crowded alkylium ions have been found.[4] In the reaction medium, the

alkene (9) remaining after fragmentation undergoes immediate protonation and the electrofugal group Me₃C⁺ is trapped by solvent, giving rise to the observed products.

The identity of the rearranged cation (10) was established as follows. The alcohol (11) was prepared, albeit in very low yield, by the reaction of 2-acetyl-1-t-butylferrocene [5] with isopropylmagnesium bromide, and this compound underwent ready acid-promoted dehydration to give a mixture of the isomeric alkenes (12) and (13). The ¹H n.m.r. signals of the cation (10), prepared unambiguously by dissolution of (11), (12), or (13) in trifluoroacetic acid were identical with those present in the spectrum of the original mixture of cations formed from (6). Furthermore, the solution of this mixture in trifluoroacetic acid was quenched with aqueous sodium hydrogen carbonate and the resulting mixture of alkenylferrocenes was separated by preparative t.l.c. The alkenes (8) and (9) [from deprotonation of (7)] and (12) and (13) [from deprotonation of (10)] were thereby obtained and were identical with authentic samples prepared by dehydration of the alcohols (3) and (11).

The surprising rearrangement of the cation (6) to the cation (10) suggested that, during the fragmentation of the former, the electrofugal group Me₃C⁺ may be trapped by the ferrocenyl residue if not by a solvent molecule. We therefore wished to establish that this process involved only a ring carbon atom (C-2 or -5) adjacent to the formal charged centre in the cation (6). Accordingly, the alcohols (17a and b) were prepared by the addition of methyl-lithium to the corresponding ketones (16a and b), which in turn were obtained by Friedel–Crafts isobutyrylation of t-butylferrocene. These alcohols were also dehydrated to give samples of the corresponding isomeric alkenes (19a and b) and (20a and b). No evidence was found for the presence of these alkenes in the mixture of products obtained previously from (6) by rearrangement and quenching. The ¹H n.m.r. spectra of the cations (18a and b) were also recorded by using solutions of the alcohol precursors (17a and b), respectively, in trifluoroacetic acid; these were distinct from that of the isomer (10) (see Table 2). Again, no evidence was found for the presence of the cations (18a or b) in the mixture of cationic products formed from the cation (6). On the basis of these experiments, we are confident that the 2-t-butyl-substituted cation (10) is the sole product of rearrangement of the cation (6).

Although the cation (10) proved relatively long-lived in trifluoroacetic acid, further slow rearrangement to the secondary cation (14) occurred. Complete conversion required ca. 48 h at 33° or ca. 8 h at 65°. When this solution was quenched with aqueous sodium hydrogen carbonate, the cation (14) was converted into the alcohol (15), which was isolated and characterised. Unfortunately, we were unable to

prepare (15) by an independent route. However, the isomers (22a and b) were synthesised by reduction with lithium aluminium hydride of the corresponding ketones (21a and b), obtained by Friedel–Crafts pivaloylation of t-butylferrocene. The spectral properties of
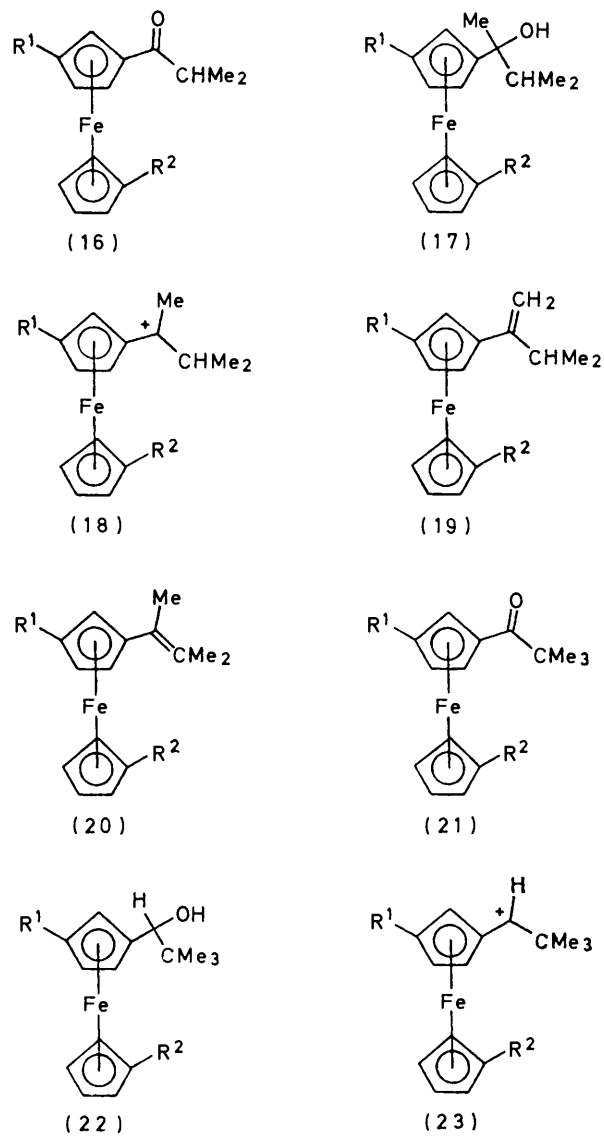
a; R¹ = CMe₃, R² = H
b; R¹ = H, R² = CMe₃

these alcohols were different from those of the alcohol (15) previously isolated. Again, the ¹H n.m.r. spectral patterns of the three isomeric cations (14), (23a), and (23b) (see Table 2), recorded for solutions in trifluoroacetic acid of the corresponding alcohols (15), (22a), and (22b), were clearly distinguishable from each other.

In an earlier investigation,[6] we had found that the reverse of the rearrangement (10) ⟶ (14) occurs in

⁵ R. A. Benkeser, Y. Nagai, and J. Hooz, J. Amer. Chem. Soc., 1964, **86**, 3742.

⁶ T. D. Turbitt and W. E. Watts, J. Organometallic Chem., 1973, **57**, C78.

trifluoroacetic acid in the absence of the ring t-butyl substituent [*i.e.* (23; $R^1 = R^2 = H$) ⟶ (18; $R^1 = R^2 = H$)]. The driving force for the latter process was attributed to the gain in thermodynamic stability associated with the conversion of a secondary into a tertiary ferrocenylalkylium ion (*cf.* pK_{R^+} values [7]). However, we had also shown that *tertiary* ferrocenyl-alkylium ions (Fc$\overset{+}{C}R^1R^2$) are destabilised by the introduction of a 2-alkyl ring substituent.[7] In the present

C-2 during rearrangement to (25) and thence to (10) by prototropic shift or deprotonation–reprotonation.

EXPERIMENTAL

For general details, see Part IV.[3]

3-*Ferrocenyl*-2,2,4,4-*tetramethylpentan*-3-*ol*   (1).—This alcohol, prepared by the method of Hon and Tidwell,[8] was obtained as red prisms (from pentane), m.p. 70—71° (lit.,[2] 75·4—76·3°), τ 5·8—5·9 (9H, m, ferrocenyl), 8·37br (1H, s, OH), and 8·87 (18H, s, CMe₃).

TABLE 2

¹H N.m.r. spectra (τ values) of t-butylferrocenylalkylium ions Me₃C(C₁₀H₈Fe)$\overset{+}{C}$XY [a]

Cation	X	Y	Cyclopentadienyl resonances [b,c]			Other resonances [b]		
			α-H	β-H	1'-H	Me₃C	X	Y [d]
(10)	Me	CHMe₂	5·42(dd)	3·66(dd), 4·05(t)	5·08(s)	8·62(s)	7·52 (s, Me)	8·45, 8·67 (2 × d, CH*Me₂*)
(14)	H	CMe₃	4·9—5·05	3·7—4·0	4·78(s)	8·76(s)	2·36 (s, H)	8·51 (s, CMe₃)
(18a)	Me	CHMe₂	4·9—5·1	3·6—3·8	5·05(s)	8·67(s)	7·98 (s, Me)	8·52, 8·77 (2 × d, CH*Me₂*)
(18b)	Me	CHMe₂	4·95(t)	3·62(t)	5·0—5·25	8·88(s)	8·01 (s, Me)	8·48, 8·72 (2 × d, CH*Me₂*)
(23a)	H	CMe₃	4·9—5·0, 5·5—5·75	3·6—3·8	4·82(s)	8·55(s)	2·71 (s, H)	8·60, 8·63 (2 × s, CMe₃) [e]
(23b)	H	CMe₃	4·35—4·5, 5·5—5·7	3·67(t)	4·7—5·2	8·84(s)	2·78 (s, H)	8·55 (s, CMe₃)

a–c See Table 1.   *d* The CH*Me₂* resonances appear as complex multiplets in the range τ 6·9—7·5.   *e* Two conformational isomers of this cation are present in solution (*cf.* ref. 3).
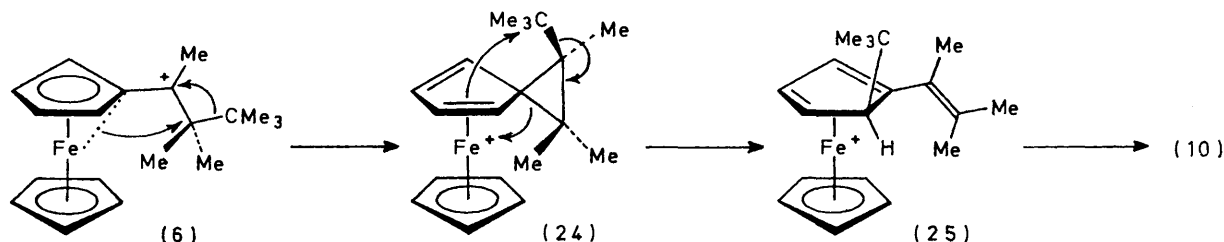
SCHEME 2   Only one enantiomeric form of the cations (24) and (25) is shown

situation, therefore, it appears that destabilisation of the cation (10) resulting from steric compression between the proximate t-butyl and $\overset{+}{C}$Me·CHMe₂ groups is such that this cation is thermodynamically less stable than the rearranged secondary cation (14) in which this effect is absent.

The transformations (5) ⟶ (6) ‡ and (10) ⟶ (14) are further examples of the double-shift rearrangement of ferrocenylalkylium ions which we reported [6] previously and whose mechanism is under further investigation. The exclusive formation of the 2-t-butyl-substituted product in the rearrangement (6) ⟶ (10) requires that the t-butyl group must be released from the precursor in close proximity to C-2 of the adjacent five-membered ring. A suprafacial [1,7] shift with retention of configuration at the migrating group, giving (25) directly, is stereochemically feasible but would require that the symmetry-forbidden nature of the process is overcome through metal-orbital involvement. An alternative mechanism is given in Scheme 2. The t-butyl group of the proposed spiro-diene intermediate [6,8] (24) is sited in ideal position for migration to

2-*Ferrocenyl*-3-*methylbutan*-2-*ol* (3).—This alcohol, prepared by the addition of methyl-lithium to 1-ferrocenyl-2-methylpropan-1-one,[9] was obtained as yellow needles (from pentane), m.p. 44—46° (lit.,[2] liquid), τ 5·7—5·9 (9H, m, ferrocenyl), 7·85 (1H, s, OH), 7·9—8·5 (1H, m, CH), 8·55 (3H, s, *Me*COH), and 9·13 and 9·32 (3H and 3H, 2 × d, CH*Me₂*).

2-*Ferrocenyl*-3-*methylbut*-1- *and* -2-*enes* [(8) *and* (9)].—The alcohol (3) (1·35 g, 5 mmol), dissolved in trifluoroacetic acid (5 ml), was stirred for 5 min and then poured into saturated aqueous sodium hydrogen carbonate. The mixture was extracted with ether and the extract was washed (H₂O), dried (MgSO₄), and evaporated. The residue was separated by preparative t.l.c. (SiO₂) with pentane as solvent. The *alkene* (8) (0·65 g, 52%) was thereby obtained as an orange liquid (Found: C, 70·9; H, 7·0. C₁₅H₁₈Fe requires C, 70·9; H, 7·1%), τ 4·70 and 5·00 (1H and 1H, 2 × d, vinyl), 5·55 and 5·75 (2H and 2H, 2 × t, C₅H₄), 5·90 (5H, s, C₅H₅), 7·0—7·6 (1H, m, CH), and 8·82 (6H, d, CH*Me₂*). The alkene (9) (0·34 g, 26%) was similarly obtained as an orange solid (from pentane), m.p. 45—47° (lit.,[2] 46—48·5°), τ 5·8—5·85 (4H, m, C₅H₄), 5·86 (5H, s, C₅H₅), and 7·96br and 8·25br (3H and 6H, 2 × s, Me).

2-*Ferrocenyl*-3,4,4-*tetramethylpent*-1-*ene* (2).—This alkene, prepared (47%) from the alcohol (1) by the method

‡ Footnote as on page 116.

[7] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 185.

[8] *Cf.* M. J. Nugent, R. E. Carter, and J. H. Richards, *J. Amer. Chem. Soc.*, 1969, **91**, 6145.

[9] R. J. Stephenson, B.P. 846,197 (*Chem. Abs.*, 1961, **55**, 17,647).

of Hon and Tidwell,[2] was obtained as a dark orange liquid (lit.,[2] oil), τ 4·12 and 4·76 (1H and 1H, 2 × d, vinyl), 5·78 (2H, m) and 5·95br (7H, s) (ferrocenyl), 8·94 (6H, s, CMe₂), and 9·23 (9H, s, CMe₃).

3-*Methyl*-2-(2-*t*-*butylferrocenyl*)*butan*-2-*ol* (11).—A solution of 2-acetyl-t-butylferrocene[5] (0·80 g, 2·8 mmol) in benzene (20 ml) was added to a solution of isopropyl-magnesium bromide [from isopropyl bromide (12·3 g, 0·1 mol)] in refluxing (70°) benzene–ether (50 ml). The mixture was heated under reflux for 60 h, then cooled, and poured cautiously into water. The organic layer was separated and combined with several ethereal extracts of the aqueous layer. The total extract was washed (H₂O), dried (MgSO₄), and evaporated. The residue was separated by preparative t.l.c. (SiO₂) with light petroleum–ether (35 : 1) as solvent. The *alcohol* (11) (29 mg, 3%) was thereby obtained as yellow-orange needles (from pentane), m.p. 68—69° (Found: C, 69·5; H, 8·5. C₁₉H₂₈FeO requires C, 69·5; H, 8·6%), τ 5·77 (5H, s, C₅H₅), 5·8—6·0 (3H, m, C₅H₃), 7·5—8·1 (1H, m, CH), 7·70 (1H, s, OH), 8·64 (12H, s, *Me*COH and CMe₃), and 8·97 and 9·44 (3H and 3H, 2 × d, CH*Me₂*). The major product of this reaction was 2-*ethyn-yl-t-butylferrocene* * (0·49 g, 68%), obtained as an orange-yellow liquid (Found: C, 72·3; H, 6·7. C₁₆H₁₈Fe requires C, 72·2; H, 6·8%), ν_{max.} (CCl₄) 2110 cm⁻¹ (C≡C), τ 5·66 (1H, t) and 6·00 (2H, d) (C₅H₃), 5·87 (5H, s, C₅H₅), 7·26 (1H, s, C≡CH), and 8·65 (9H, s, CMe₃).

Isobutyrylation of t-Butylferrocene.—A Perrier complex of isobutyryl chloride (7·95 g, 75 mmol) and aluminium chloride in dichloromethane (100 ml) was added to a solution of t-butylferrocene[10] (12·1 g, 50 mmol) in dichloromethane (100 ml). The resulting purple solution was stirred for 20 h and then poured into water. The organic material was extracted by conventional work-up procedures. The product consisted of a complex mixture of ketonic compounds from which the required derivatives were separated by repeated column (Al₂O₃) and thin-layer (SiO₂) chromatography. 2-*Methyl*-1-(3-*t*-*butylferrocenyl*)-*propan*-1-*one* (16a) (1·1 g, 8%) was obtained as deep orange plates (from pentane), m.p. 68—70° (Found: C, 69·5; H, 7·8. C₁₈H₂₄FeO requires C, 69·2; H, 7·8%), τ 5·25 and 5·58 (2H and 1H, 2 × m, C₅H₃), 5·80 (5H, s, C₅H₅), 6·6—7·2 (1H, m, CH), 8·70 (9H, s, CMe₃), and 8·80 (6H, d, CH*Me₂*). 2-*Methyl*-1-(1′-*t*-*butylferrocenyl*)*propan*-1-*one* (16b) (0·9 g, 7%) was obtained as a deep orange liquid (Found: C, 69·3; H, 7·6%), τ 5·27 and 5·56 (2H and 2H, 2 × t, C₅H₄CO), 5·85—6·15 (4H, m, C₅*H*₄CMe₃), 6·7—7·2 (1H, m, CH), 8·83 (9H, s, CMe₃), and 8·84 (6H, d, CH*Me₂*).

Pivaloylation of t-Butylferrocene.—Finely ground aluminium chloride (1·5 g, 5·6 mmol), followed immediately by a solution of pivaloyl chloride (1·3 g, 10 mmol) in dichloromethane (10 ml), was added to a stirred solution of t-butylferrocene[10] (2·42 g, 10 mmol) in dichloromethane (100 ml) at 0°. The dark blue solution was stirred for 15 min and then worked up as in the preceding experiment. The following compounds were separated from the product mixture by preparative t.l.c. (SiO₂): t-butylferrocene (0·78 g, 32% recovery); 2,2-*dimethyl*-1-(3-*t*-*butylferrocenyl*)*pro-pan*-1-*one* (21a) (0·56 g, 25%), a deep orange solid (from pentane), m.p. 107—108° (Found: C, 70·1; H, 7·9. C₁₉-H₂₆FeO requires C, 70·0; H, 8·0%), τ 5·29 and 5·73 (2H and 1H, 2 × m, C₅H₃), 5·92 (5H, s, C₅H₅), and 8·75 and

8·83 (9H and 9H, 2 × s, CMe₃); 2,2-*dimethyl*-1-(1′-*t*-*butyl-ferrocenyl*)*propan*-1-*one* (21b) (0·54 g, 24%), deep orange plates (from pentane), m.p. 61—63° (Found: C, 70·1; H, 7·9%), τ 5·16 and 5·56 (2H and 2H, 2 × t, C₅H₄CO), 5·85—6·05 (4H, m, C₅*H*₄CMe₃), and 8·69 and 8·81 (9H and 9H, 2 × s, CMe₃).

3-*Methyl*-2-(3-*t*-*butylferrocenyl*)*butan*-2-*ol* (17a).—This *alcohol*, prepared by the addition of methyl-lithium to the ketone (16a), was obtained as a dark orange liquid (Found: C, 69·7; H, 8·6. C₁₉H₂₈FeO requires C, 69·5; H, 8·6%), τ 5·80 (5H, s, C₅H₅), 5·8—6·2 (3H, m, C₅H₃), 7·82br (1H, s, OH), 8·2—8·7 (1H, m, CH), 8·55 (3H, s, *Me*COH), 8·79 (9H, s, CMe₃), and 9·12 and 9·31 (3H and 3H, 2 × d, CH*Me₂*).

The *alcohol* (17b), similarly prepared from the ketone (16b), was obtained as a dark orange liquid (Found: C, 69·8; H, 8·7%), τ 5·6—6·0 (8H, m, ferrocenyl), 7·78br (1H, s, OH), 8·0—8·6 (1H, m, CH), 8·53 (3H, s, *Me*COH), 8·77 (9H, s, CMe₃), and 9·11 and 9·30 (3H and 3H, 2 × d, CH*Me₂*).

2,2-*Dimethyl*-1-(3-*t*-*butylferrocenyl*)*propan*-1-*ol* (22a).—This *alcohol*, prepared by reduction of the ketone (21a) with lithium aluminium hydride, was obtained as an orange-yellow liquid (Found: C, 69·8; H, 8·6. C₁₉H₂₈FeO requires C, 69·5; H, 8·6%), τ 5·78 (5H, s, C₅H₅), 5·8—6·05 (4H, m, C₅H₃ + CH), 7·90br (1H, s, OH), and 8·80 and 9·16 (9H and 9H, 2 × s, CMe₃).

The *alcohol* (22b), similarly prepared from the ketone (21b), was obtained as orange-yellow plates (from pentane), m.p. 94—96° (Found: C, 69·5; H, 8·6%), τ 5·65—6·0 (9H, m, ferrocenyl + CH), 7·87br (1H, s, OH), and 8·78 and 9·14 (9H and 9H, 2 × s, CMe₃).

3-*Methyl*-2-(3-*t*-*butylferrocenyl*)*but*-1- *and* -2-*enes* [(19a) *and* (20a)].—The alcohol (17a) was dehydrated by successive treatment with trifluoroacetic acid and aqueous sodium hydrogen carbonate as described in a previous experiment. The products were separated by preparative t.l.c. (SiO₂) with light petroleum as solvent. The *alkene* (19a) was obtained as an orange-yellow liquid (Found: C, 73·5; H, 8·5. C₁₉H₂₆Fe requires C, 73·6; H, 8·5%), τ 4·79 and 5·09 (1H and 1H, 2 × m, vinyl), 5·71 and 5·84 (2H and 1H, 2 × m, C₅H₃), 5·97 (5H, s, C₅H₅), 7·1—7·7 (1H, m, CH), 8·80 (9H, s, CMe₃), and 8·85 (6H, d, CH*Me₂*). The *alkene* (20a) was obtained as an orange-yellow liquid (Found: C, 73·5; H, 8·5%), τ 5·71 and 5·84 (2H and 1H, 2 × m, C₅H₃), 5·90 (5H, s, C₅H₅), 7·99br, 8·23br, and 8·29br (each 3H, 3 × s, Me), and 8·80 (9H, s, CMe₃).

3-*Methyl*-2-(1′-*t*-*butylferrocenyl*)*but*-1- *and* -2-*enes* [(19b) *and* (20b)].—The alcohol (17b) was dehydrated by the same method. The *alkene* (19b) was obtained as an orange liquid (Found: C, 73·5; H, 8·4. C₁₉H₂₆Fe requires C, 73·6; H, 8·5%), τ 4·79 and 5·09 (1H and 1H, 2 × m, vinyl), 5·85—6·05 (8H, m. ferrocenyl), 7·1—7·7 (1H, m, CH), 8·80 (9H, s, CMe₃), and 8·84 (6H, d, CH*Me₂*). The *alkene* (20b) was obtained as an orange liquid (Found: C, 73·5; H, 8·4%), τ 5·65—6·0 (8H, m, ferrocenyl), 7·96br and 8·26br (3H and 6H, 2 × s, Me), and 8·80 (9H, s, CMe₃).

3-*Methyl*-2-(2-*t*-*butylferrocenyl*)*but*-1- *and* -2-*enes* [(12) *and* (13)].—The alcohol (11) was dehydrated by the same method. The *alkene* (12) was obtained as an orange-yellow liquid (Found: C, 73·7; H, 8·3. C₁₉H₂₆Fe requires C, 73·6; H, 8·5%), τ 4·59 and 4·82 (1H and 1H, 2 × d, vinyl), 5·81 (5H, s, C₅H₅), 5·97 and 6·14 (2H and 1H, 2 × m,

* The application of this alkyne synthesis to other sterically hindered acylferrocenes will be described in a forthcoming publication, in which the mechanism of the reaction will be discussed.

[10] T. S. Abram and W. E. Watts, *Synth. in Inorg. and Metal-Org. Chem.*, 1974, **4**, 335.

C_5H_3), 7·2—7·7 (1H, m. CH), 8·75 (9H, s, CMe$_3$), and 8·85 and 9·04 (3H and 3H, 2 × d, CHMe$_2$). The *alkene* (13) was obtained as an orange-yellow liquid (Found: C, 73·6; H, 8·3%), τ 5·84 (5H, s, C_5H_5), 5·99 and 6·22 (2H and 1H, 2 × m, C_5H_3), 7·76br, 8·30br, and 8·76br (each 3H, 3 × s, Me), and 8·79 (9H, s, CMe$_3$).

2,2-Dimethyl-1-(2-t-butylferrocenyl)propan-1-ol (15).—A solution of a mixture of the alkenes (12) and (13) (0·5 g, 1·6 mmol) in trifluoroacetic acid (10 ml) was stirred under nitrogen at 65° for 12 h, and then poured into an excess of saturated aqueous sodium hydrogen carbonate. The product was extracted with ether. Chromatography (Al$_2$O$_3$) afforded the *alcohol* (15) (0·3 g, 58%), which was obtained as yellow needles (from pentane), m.p. 50—51° (Found: C, 69·7; H, 8·6. $C_{19}H_{28}FeO$ requires C, 69·5; H, 8·6%), τ 5·4—5·9 (4H, m, C_5H_3 + CH), 5·90 (5H, s,

[11] A. C. Pierce and M. M. Jouillié, *J. Org. Chem.*, 1962, **27**, 3968.

C_5H_5), 7·86br (1H, s, OH), and 8·62 and 8·81 (9H and 9H, 2 × s, CMe$_3$).

t-Butyl Trifluoroacetate.—A solution of t-butyl alcohol (1·85 g, 25 mmol) in trifluoroacetic acid (20 ml) was stirred for 48 h. The solution was diluted with dichloromethane (20 ml) with rapid stirring and cooling, and sufficient deactivated alumina was added to remove the excess of acid by adsorption. The mixture was filtered and fractionally distilled, affording the ester, b.p. 82—83° (lit.,[11] 83°), $\nu_{max.}$ (CH$_2$Cl$_2$) 1779 cm^{-1} (C=O), τ (CF$_3$·CO$_2$H) 8·40 (s, CMe$_3$), which was unstable at its b.p. but could be stored in dichloromethane in a refrigerator.