Acid-induced Reactions of 1-Cyclopropyl-1-ferrocenyl-ethanols and -methanols [1]

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The reactions of some 1-cyclopropyl-1-ferrocenyl-ethanols and -methanols under mild acidic conditions are described. The stereospecific ring opening observed in some cases is rationalized in terms of a preferred conformation of the bisected carbocation. The influence of substituents upon the reaction is discussed.

IN an earlier study [2] difficulty was encountered in the synthesis of 1-ferrocenyl-1-cyclopropylethylenes by the Wittig reaction from the corresponding ketones. The reason for the low yield from such reactions was probably steric hindrance to the approach of the ylide at the carbonyl carbon atom. An alternative approach to the olefins was employed, involving acid-induced dehydration (H_2SO_4–H_2O–C_6H_6) of alcohols. Under these conditions the alcohol (1) gave the olefin (2) in reasonable yield. A milder variant of this, chromatography on silica gel, was also extremely successful.† The ease with which such dehydrations take place in the ferrocenyl systems is related to the known stability of ferrocenylmethylium ions.[4] The reaction of the alcohol (3) under the acidic conditions used previously did not yield an olefin, giving only the ether (4).[2] The formation of this ether was again evidence for the formation of a ferrocenylmethylium ion; however, in this instance, deprotonation did not compete with trapping of the ion by another molecule of alcohol. This result could be due to a concentration effect. Nevertheless it was surprising to find that neither ion (5) nor (6) [from the alcohols (1) and (3), respectively] appeared to undergo cyclopropane ring opening, especially in the light of later work by Watts.[5] The literature has many examples [6] of such processes in non-ferrocenyl systems, and Mechtler and Schlögl [7] have reported the conversion of 2-ferrocenylcyclopropanecarboxylic acid into 4-ferrocenyl-4-butyrolactone by treatment with polyphosphoric acid. In view of the foregoing, the behaviour of the alcohols merited closer study.

† A method for the dehydration of ferrocenylmethanols with acidic alumina has been described previously.[3]

[1] Preliminary report, W. M. Horspool and B. J. Thomson, *Tetrahedron Letters*, 1974, 3529.

[2] W. M. Horspool, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc.* (*C*), 1971, 1558.

[3] K. Schlögl and A. Mohar, *Monatsh.*, 1961, **92**, 219; *Naturwiss'*, 1961, **48**, 376.

The five cyclopropyl-substituted alcohols (3) and (7)—(10) were readily synthesized from the corresponding ketones (11a—c) by reaction with lithium aluminium
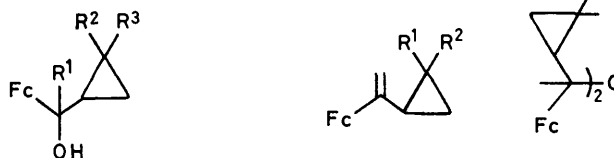
(1) R^1=Me, R^2=R^3=H
(3) R^1=R^2=R^3=Me
(7) R^1=R^2=R^3=H
(8) R^1=H, R^2=R^3=Me
(9) R^1=R^2=H, R^3=Ph
(10) R^1=Me, R^2=H, R^3=Ph

(2) R^1=R^2=H
(15) R^1=H, R^2=Ph
(16) R^1=R^2=Me

(4)
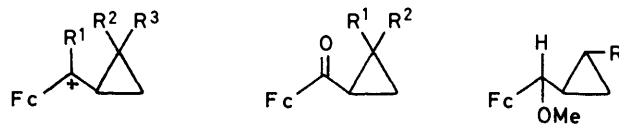
(5) R^1=Me, R^2=R^3=H
(6) R^1=R^2=R^3=Me
(14) R^1=R^2=R^3=H

(11) a; R^1=R^2=H
b; R^1=R^2=Me
c; R^1=H, R^2=Ph

(12) R =H
(13) R =Ph

hydride (or sodium borohydride) or with methyllithium. The original dehydration experiment [2] with acid (H_2SO_4–C_6H_6–H_2O) was thought to be too drastic, and the milder system (silica gel) was used as the source of acid. The silica gel was used either with the alcohol dissolved in methanol or ethanol at reflux, or as the substrate for column chromatography.

The former system (silica gel–alcohol) was used for

[4] M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

[5] W. E. Watts, *J.C.S. Perkin I*, 1976, 804.

[6] C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, 1970, **92**, 4274; C. D. Poulter and S. Winstein, *ibid.* p. 4282; C. D. Poulter and C. J. Spillner, *ibid.*, 1974, **96**, 7591.

[7] H. Mechtler and K. Schlögl, *Monatsh.*, 1966, **97**, 754.

the quantitative conversion of the alcohols (7) and (9) into the methyl ethers (12) and (13), respectively, thus again demonstrating the ease of generation of ferrocenylmethylium ions. The ¹H n.m.r. spectrum of the crude mixtures from both these reactions showed no trace of ring-opened products. This absence of ring-opening for the alcohol (7) is in agreement with its behaviour in trifluoroacetic acid; the n.m.r. spectrum of the species generated is without doubt that of the ion (14).[5]* Introduction of a single phenyl group into the cyclopropane ring does not influence the ring opening to any measurable extent. The situation is changed dramatically when a methyl group is present at the α-carbon atom.

The alcohol (10) was chromatographed on silica gel (for exact conditions see Experimental section). This led to isolation of the olefin (15) and the ring-opened compound (16). Ring opening was also found when the alcohol (10) was treated in refluxing ethanol with silica gel, giving the ether (17). The alcohol (3) also undergoes ring-opening reactions, giving the hydroxy-olefin (19) in high yield as well as a trace of the olefin (18).

The ring-opened compounds (16), (17), and (19) are all represented in the E-form. No trace of the Z-isomer was ever detected.† Thus it is likely that the ring-opening process is stereospecific. There are many examples [6] of such stereospecificity in non-ferrocenyl systems. The assignment of the E-configuration to the isomer isolated is based solely on the n.m.r. allylic coupling constants of ca. 1.6 Hz. Such coupling, although not definitive for a trans-arrangement of the methyl group and the proton, agrees well with literature values.[8] In the absence of the Z-isomers, we had no indication of what coupling constants such compounds would exhibit. To resolve the situation the reactions of the alcohol (8) were studied in the hope that a clear distinction between E- and Z-isomer coupling constants would be obtained in this instance. This was expected since we would be measuring normal vinylic H,H-coupling, where the distinctions are often greater (6—12 Hz for Z; 12—18 Hz for E),[9] ‡ than for allylic coupling where it is not unknown for the Z- and E-isomers to have the same J value.[8]

The alcohol (8) underwent ring opening cleanly upon chromatography to afford the diene (20) and the alcohol (21). The coupling constant for each of these compounds was 15.5 Hz, in agreement with an E-configuration. Again there was no evidence for the formation of the Z-isomer. The fact that there had been no structural rearrangement during ring opening was checked by catalytic reduction of the diene (20) to give

the alkane (22). The alcohol (8) also reacted cleanly with methanol–silica gel to yield the ether (23), again as the E-isomer.

These latter experiments confirmed that the ring opening was stereospecific, within the sensitivity of the analytical method. This is in accord with current thinking on the ring opening of such cyclopropyl-methylium ions, involving a bisected form of the ion,[6] shown by n.m.r. spectroscopy to be the most stable
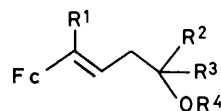
(16) R¹=Me, R²=R⁴=H,R³=Ph
(17) R¹=Me,R²=H,R³=Ph,R⁴=Et
(19) R¹=R²=R³=Me,R⁴=H
(21) R¹=R⁴=H,R²=R³=Me
(23) R¹=H,R²=R³=R⁴=Me
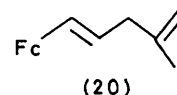
(20)
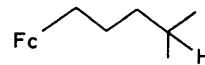
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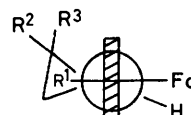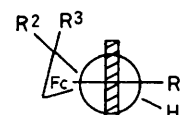
(24)   (25)
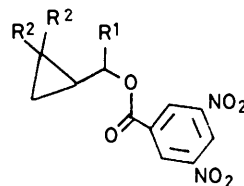
(26) R¹=Me,R²=H
(27) R¹=H,R²=Me

arrangement. In this conformation the vacant p-orbital of the ionic centre is parallel with the cyclopropane ring.[10] This evidence and more recent work by Kelly and Brown [11] have confirmed that σ bridging (a non-classical ion) is not important in such systems. Calculations have also confirmed the stability of the bisected form over the perpendicular arrangement, although no agreement has been reached as to the specific energy difference, values for which have ranged from 9 to 41 kcal mol⁻¹ (37.7 to 171.8 kJ mol⁻¹).[12] It is

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* We are indebted to Dr. W. E. Watts, Department of Chemistry, The New University of Ulster, Coleraine, for supplying this information prior to publication of ref. 5.

† If the Z-isomer were formed, acid-catalysed isomerization to the E-isomer might take place. However, careful examination of the reaction mixture after a variety of reaction times showed no evidence for the presence of the Z-isomer.

‡ The coupling constant for E-1-ferrocenyl-2-phenylethylene is 17.5 Hz (W. M. Horspool and R. G. Sutherland, Canad. J. Chem., 1969, 46, 3453).

[8] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance,' Pergamon, Oxford, 1965, pp. 176 and 739.

[9] R. M. Silverstein, C. G. Bassler, and T. C. Morrill, ' Spectrometric Identification of Organic Compounds,' Wiley–Interscience, 1974.

[10] C. U. Pittman and G. A. Olah, J. Amer. Chem. Soc., 1965, 87, 5123; D. S. Kabaloff and E. Namanworth, ibid., 1970, 92, 3234; G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, ibid., 1972, 94, 147.

[11] D. P. Kelly and H. C. Brown, J. Amer. Chem. Soc., 1975, 97, 3897.

[12] R. Hoffmann, J. Chem. Phys., 1964, 40, 2480; L. Radom, J. A. Pople, V. Buss, and P. von R. Schleyer, J. Amer. Chem. Soc., 1970, 92, 6380; W. C. Danen, ibid., 1972, 94, 4835.

clear that cyclopropyl groups can play a major role in the stabilization of carbocations, and that the magnitude of the role is dependent on the geometric set-up.[13] The intermediate carbocation [e.g. (6)] can adopt two possible bisected forms, (24) and/or (25). In representation (24) steric interactions are less than in (25) where the ferrocenyl and cyclopropyl groups are eclipsed; thus the former is preferred. Ring opening within a representation such as (24) gives rise to the observed E-configuration in the product. The absence of the Z-isomer indicates a strong preference for the conformation shown in (24).

The ring opening of compounds (3) and (10) shows that the greatest effect is found in the introduction of an electron-donating substituent, in addition to the ferrocene, at the cationic site. Methyl groups at such a position have previously been shown to have a dramatic effect on the solvolytic behaviour of (26), which is solvolysed 1 000 times faster than the parent compound.[14] Furthermore the 1-cyclopropyl-1-methylethylium ion has been calculated to be 30 kcal mol^{-1} more stable than cyclopropylmethylium.[15] However under the conditions used by us ring opening only took place where there was either substitution on the cyclopropane ring (2,2-dimethyl or 2-phenyl) or substitution at both the cationic site and the 2-position in the cyclopropane ring.[16] Solvolysis studies have shown that substituents in the cyclopropane ring have a marked although smaller effect than substitution at the cationic site. Thus the 2,2-dimethyl derivative (27) is solvolysed 92 times faster than the parent,[16] and the smallest effect is found with a *trans*-2-phenyl group, where the enhancement factor is only 2.2.[17] Thus our results fit into the general scheme previously established for cyclopropylmethylium ions in the non-ferrocenyl series.

EXPERIMENTAL

2,2-Dimethylcyclopropyl(ferrocenyl)methanol (8).—Lithium aluminium hydride (2.0 g) was added to ether (50 ml; anhydrous) and the mixture was refluxed for 1 h. 2,2-Dimethylcyclopropyl ferrocenyl ketone [1] (4.0 g) in ether (150 ml; anhydrous) was added slowly to the refluxing solution. The whole solution was refluxed for 7 h, then cooled, and ethyl acetate was added. The mixture was poured into water and extracted with ether. The extracts were washed with water and saturated sodium hydrogen carbonate solution, dried (MgSO$_4$), filtered, and evaporated to dryness. The resultant yellow oil was chromatographed on alumina. Light petroleum–ether (1 : 1) eluted starting material (0.06 g), and ether eluted the *alcohol* (8) (2.8 g), which crystallised from light petroleum as dark orange prisms, m.p. 65—68°, $\nu_{max.}$ (Nujol) 3 400 cm^{-1}; τ (CCl$_4$) 5.90 (9 H, m), 6.25 (1 H, dd, J 4 and 10 Hz, collapsing to d, J 10 Hz, on addition of D$_2$O), 8.22 (1 H, d, J 4 Hz, disappears on addition of D$_2$O), 8.79 (3 H, s), 8.90 (3 H, s), and 9.0—9.9 (3 H, m) (Found: C, 67.6; H, 7.3. C$_{16}$H$_{20}$FeO requires C, 67.6; H, 7.1%).

1-(2,2-*Dimethylcyclopropyl*)-1-*ferrocenylethanol* (3).—Methyl-lithium in hexane (1.75M; 7.0 ml) was injected through a serum cap into a solution of 2,2-dimethylcyclopropyl ferrocenyl ketone (1.0 g) in ether (50 ml; anhydrous) under nitrogen. An immediate colour change from red to yellow took place, and the reaction was quenched by pouring into water. The organic material was extracted into ether and the extracts were washed with water and brine, dried (MgSO$_4$), filtered, and evaporated to dryness. The residue was chromatographed on alumina. Benzene eluted the alcohol (0.55 g), identical with authentic material.[2]

Ferrocenyl-(2-phenylcyclopropyl)methanol (9).—Lithium aluminium hydride (0.4 g) was refluxed in ether (25 ml; anhydrous) for 0.5 h ferrocenyl 2-phenylcyclopropyl ketone [2] (0.6 g) in ether (50 ml; anhydrous) was added and the mixture was refluxed for 2 h. Conventional work-up gave a yellow oil which was chromatographed on alumina. Benzene eluted the *alcohol* (9) (0.4 g) as a yellow viscous oil, $\nu_{max.}$ (film) 3 550, 3 425, 1 606, 700, and 690 cm^{-1}; τ (CCl$_4$) 2.91br (5 H, s), 5.98br (10 H, s), 7.91br (1 H, d, J 4.3 Hz, disappears on addition of D$_2$O), and 8.07—9.3 (4 H, m) (Found: C, 72.3; H, 6.3. C$_{20}$H$_{20}$FeO requires C, 72.3; H, 6.1%).

Cyclopropyl(ferrocenyl)methanol (7).—Cyclopropyl ferrocenyl ketone [2] (1.5 g) was dissolved in methanol (50 ml) and sodium borohydride (0.3 g) was added. The mixture was stirred for 0.5 h during which time the colour changed from red to yellow. The reaction was quenched by pouring into water. The organic material was extracted into ether. The extracts were washed with water, dried (MgSO$_4$), filtered, and evaporated to dryness to yield a mobile orange oil, which was chromatographed on alumina. Ether eluted the *alcohol* (7) (1.32 g), which crystallised from light petroleum–cyclohexane as pale orange needles, m.p. 44.5—46.5°; $\nu_{max.}$ (Nujol) 3 400 cm^{-1}; τ (CDCl$_3$) 5.77 (9 H, s), 6.27 (1 H, dd, J 6.9 and 4.3 Hz, transformed into a doublet, J 6.9 Hz, on addition of D$_2$O), 8.00 (1 H, d, J 4.3 Hz, disappears on addition of D$_2$O), 8.6—9.2 (1 H, m), and 9.3—9.8 (4 H, m) (Found: C, 65.5; H, 6.3. C$_{14}$H$_{16}$FeO requires C, 65.7; H, 6.3%).

1-*Ferrocenyl*-1-(2-*phenylcyclopropyl*)*ethanol* (10).—Ferrocenyl 2-phenylcyclopropyl ketone (1 g) was dissolved in ether (50 ml; anhydrous) under nitrogen, and methyl-lithium (1.75 M; 7 ml) was added from a syringe. The mixture was stirred for 1 h and then poured into water and extracted into ether. Conventional work-up and chromatography on alumina with benzene gave the *alcohol* (10) (1.0 g) as a red oil, $\nu_{max.}$ (film) 3 550 and 3 450 cm^{-1}; τ (CCl$_4$) 2.86 (5 H, m), 5.86—5.91 (9 H), 7.8—8.2 (1 H, m), 8.35br (1 H, d, disappears on addition of D$_2$O), 8.49 (3 H, s), and 8.65—9.4 (3 H, m) (Found: C, 73.6; H, 6.7. C$_{21}$H$_{22}$FeO requires C, 72.8; H, 6.4%).

Reaction of Cyclopropyl(ferrocenyl)methanol (7) *with Methanol.*—The alcohol (0.3 g) was dissolved in methanol (20 ml) and silica gel (1.2 g; MFC) was added. The mixture was refluxed for 4 h, after which t.l.c. indicated that all the starting material had reacted. The silica gel was filtered off and the filtrate was evaporated to dryness. The residue

[13] P. von R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, 1969, **91**, 5880.
[14] P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, 1966, **88**, 2321.
[15] W. J. Hehre and P. G. Hiberty, *J. Amer. Chem. Soc.*, 1974, **96**, 302.
[16] C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1973, **95**, 8192.
[17] R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 4843.

was chromatographed on alumina. Ether–light petroleum (1 : 1) eluted *methyl cyclopropyl(ferrocenyl)methyl ether* (12) (0.32 g), as a red oil, b.p. 122° at 0.6 mmHg; $\nu_{max.}$ (film) 1 085 cm^{-1}; τ (CDCl$_3$) 5.74 (2 H, t), 5.85 (7 H, s), 6.53 (1 H, d, J 6.9 Hz), 6.63 (3 H, s), 8.6—9.0 (1 H, m), and 9.2—9.8 (4 H, m) (Found: C, 66.7; H, 7.0. $C_{15}H_{18}FeO$ requires C, 66.7; H, 6.7%).

Reaction of Ferrocenyl-(2-phenylcyclopropyl)methanol (9) *with Methanol.*—The alcohol (0.3 g) was dissolved in methanol (20 ml) and silica gel (1.2 g; MCF) was added. The reaction was carried out and worked up as described above. *Methyl ferrocenyl-(2-phenylcyclopropyl)methyl ether* (13) (0.26 g) was obtained as an orange-yellow oil, b.p. 172—174° at 0.5 mmHg; $\nu_{max.}$ (film) 1 100 cm^{-1}; τ (CDCl$_3$) 2.83 (5 H, m), 5.91br (9 H, s), 6.22 (1 H, 4-line multiplet), 6.60 and 6.68 (3 H, two singlets), and 7.70—9.15 (4 H, m) (Found: C, 73.6; H, 6.9. $C_{21}H_{22}FeO$ requires C, 72.9; H, 6.4%).

Reaction of 1-Ferrocenyl-1-(2-phenylcyclopropyl)ethanol (10) *on Silica Gel.*—The alcohol (1.5 g) was added, in ether, to a silica gel column made up in ether. No reaction took place.

The alcohol (1.3 g) was added, in ether, to a silica gel column made up in light petroleum. The column became warm and elution was continued with ether. The material which eluted was rechromatographed on alumina. Light petroleum–ether (4 : 1) eluted 1-ferrocenyl-1-(2-phenyl-cyclopropyl)ethylene (15) (0.43 g, 32.7%), identical with authentic material. Light petroleum–ether (1 : 1) eluted starting material (0.29 g, 22.2%) and (E)-4-*ferrocenyl-1-phenylpent-3-en-1-ol* (16) (0.43 g, 34.9%), which crystallised from light petroleum–cyclohexane as fine orange needles, m.p. 93—95°; $\nu_{max.}$ (Nujol) 3 120 cm^{-1}; τ (CDCl$_3$) 2.73 (5 H, m), 4.43 (1 H, tq, J 7.7 and 1.7 Hz), 5.40 (1 H, t, J 7.0 Hz), 5.88 (2 H, t), 5.94 (2 H, t), 6.08 (5 H, s), 7.56 (3 H, apparent t, J 7.7 Hz; OH also under this absorption), and 8.15br (3 H, s) (Found: C, 73.4; H, 6.5. $C_{21}H_{22}FeO$ requires C, 72.8; H, 6.4%).

Reaction of the Alcohol (10) *with Ethanol.*—The alcohol (0.6 g) was dissolved in ethanol (50 ml), silica gel (2.0 g; MFC) was added, and the mixture was heated at 80 °C for 10 min. The silica was filtered off and the filtrate evaporated to dryness. The residue was chromatographed on alumina. Light petroleum–ether (11.5 : 1) eluted 1-ferrocenyl-1-(2-phenylcyclopropyl)ethylene (15) (0.26 g) followed by (E)-5-*ethoxy-2-ferrocenyl-5-phenylpent-2-ene* (17) (0.1 g) as a red oil, $\nu_{max.}$ (film) 1 100 cm^{-1}; τ (CCl$_4$) 2.70 (5 H, s), 4.41br (1 H, t, J 7.7 Hz), 5.8 (3 H, m), 5.95 (2 H, t), 6.05 (5 H, s), 6.65 (2 H, q, J 7.0 Hz), 7.52 (2 H, t, J 7.0 Hz), 8.19br (3 H, s), and 8.81 (3 H, t, J 7.0 Hz) (Found: C, 74.1; H, 7.6. $C_{23}H_{26}FeO$ requires C, 73.8; H, 7.0%).

Reaction of 1-(2,2-Dimethylcyclopropyl)-1-ferrocenylethanol (3) *on Silica Gel.*—The alcohol (0.4 g) was dissolved in ether and added to a silica gel column made up in light petroleum. Elution with ether gave a yellow material which was rechromatographed on alumina. Benzene eluted 1-(2,2-dimethylcyclopropyl)-1-ferrocenylethylene (18) (0.013 g,

3%), identical with authentic material, and benzene–ether (1 : 1) eluted (E)-5-*ferrocenyl-2-methylhex-4-en-2-ol* (19) (0.29 g, 72%), obtained as orange rosettes, m.p. 72—75° (from light petroleum); $\nu_{max.}$ (Nujol) 3 300, 910, and 880 cm^{-1}; τ (CDCl$_3$) 4.23 (1 H, tq, J 8.2 and 1.6 Hz), 5.62 (2 H, t), 5.81 (2 H, t), 5.92 (5 H, s), 7.73 (2 H, d, J 8.2 Hz), 8.02 (3 H, d, J 1.6 Hz), 8.20br (1 H, s), and 8.77 (6 H, s) (Found: C, 68.4; H, 7.5. $C_{17}H_{22}FeO$ requires C, 68.5; H, 7.4%).

Ring Opening of 2,2-Dimethylcyclopropyl(ferrocenyl)-methanol (8).—The alcohol (1.5 g) dissolved in ether (20 ml) was added to a column of silica gel made up in benzene. The column became warm, and was developed with ether, which washed the ferrocenyl material through as a single band. This material (1.4 g, 93%) was rechromatographed on alumina. Benzene eluted (E)-1-*ferrocenyl-4-methyl-penta-1,4-diene* (20) (0.49 g, 35%) as a red oil (b.p. 180° at 10 mmHg); $\nu_{max.}$ (film) 1 650 cm^{-1}; τ (CCl$_4$) 3.89 (1 H, d, J 15.5 Hz), 4.0—4.55 (1 H, dt, J 15.5 and 6 Hz), 5.26br (2 H, s), 5.80 (2 H, t), 5.90—6.01 (7 H, m), 7.29 (2 H, d, J 6 Hz), and 8.25br (3 H, s) (Found: C, 71.0; H, 6.7. $C_{16}H_{18}Fe$ requires C, 72.2; H, 6.8%). Light petroleum–ether (1 : 1) eluted starting material (0.42, 28%), and ether eluted (E)-5-*ferrocenyl-2-methylpent-4-en-2-ol* (21) (0.42 g, 28%), m.p. 81.5—83.5° (yellow crystals from light petroleum); $\nu_{max.}$ (Nujol) 3 320 and 905 cm^{-1}; τ (CCl$_4$) 3.85 (1 H, d, J 15.5 Hz), 4.0—4.50 (1 H, dt, J 15.5 and 6 Hz), 5.78 (2 H, t), 5.90 (2 H, t), 6.01 (5 H, s), 7.83 (2 H, d, J 6 Hz), 8.67 (1 H, s), and 8.82 (6 H, s) (Found: C, 67.5; H, 7.0. $C_{16}H_{20}FeO$ requires C, 67.6; H, 7.1%).

Reduction of (E)-1-*Ferrocenyl-4-methylpenta-1,4-diene* (20). —The diene (0.37 g) dissolved in cyclohexane containing palladium–carbon (0.15 g, 30%) was hydrogenated at atmospheric pressure. Reduction (70 ml uptake) was complete after 0.5 h and the colour of the solution had changed from wine-red to yellow. Conventional work-up gave 1-*ferrocenyl-4-methylpentane* (22) (0.3 g) as an orange oil, b.p. 160—162° at 4 mmHg; τ (CCl$_4$) 6.02 (9 H, m), 7.72 (2 H, t, J 6.9 Hz), 8.2—8.9 (5 H, m), and 9.13 (6 H, d, J 6 Hz) (Found: C, 70.8; H, 8.3. $C_{16}H_{22}Fe$ requires C, 71.1; H, 8.2%).

Reaction of 2,2-Dimethylcyclopropyl(ferrocenyl)methanol (8) *with Methanol.*—The alcohol (0.3 g) was dissolved in methanol (20 ml). Silica gel (1.2 g; MFC) was added and the mixture was heated at reflux for 2.5 h, during which time it changed colour from orange to red. The mixture was filtered and evaporated to dryness, and the residue was chromatographed on alumina. Benzene eluted the main component as a red oil, identified as (E)-1-*ferrocenyl-4-methoxy-4-methylpent-1-ene* (23) (0.29 g, 91%), b.p. 128—130° at 0.5 mmHg; $\nu_{max.}$ (film) 1 080 and 965 cm^{-1}; τ (CDCl$_3$) 3.84 (1 H, d, J 15.5 Hz), 4.1 (1 H, dt, J 15.5 and 6.0 Hz), 5.70 (2 H, t), 5.86 (2 H, t), 5.92 (5 H, s), 6.77 (3 H, s), 7.76 (2 H, d, J 6.0 Hz), and 8.83 (6 H, s) (Found: C, 68.5; H, 7.5. $C_{17}H_{22}FeO$ requires C, 68.5; H, 7.4%).