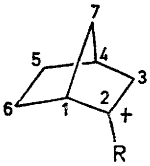
Stable Carbonium Ions. Part I. 2-Ferrocenylnorbornan-2-yl Cation

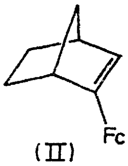
By **M. J. A. Habib** and **W. E. Watts,*** Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow C.1

The 2-ferrocenylnorbornan-2-yl cation is formed quantitatively on treatment of either 2-ferrocenylnorborn-2-ene or the 2-ferrocenylnorbornan-2-ol epimers with protic acids. The cation, which may also be generated under aprotic conditions by abstraction of hydroxide from the norbornanols using triphenylmethyl tetrafluoroborate, undergoes proton elimination in preference to addition reactions, shows no tendency towards skeletal or hydride-shift rearrangement, but is reversibly converted into a new species in strongly acidic media (>80% H_2SO_4 aq.). The ^1H n.m.r. and electronic spectra of the cation and of methylferrocenyl analogues are discussed.

DESPITE a prodigious volume of experimental work, the structure of the norbornan-2-yl and related cations remains in dispute.[1] In the case of the tertiary 2-substituted species (I), it is a key tenet of nonclassical theory [1a] that, the greater the ability of the substituent (R) to stabilise an electron-deficient centre, the smaller demand there will be for participation by the σ-electrons of the C(1)–C(6) bond; *i.e.* the distribution of positive charge to C(1) in cations of this type is diminished as the electron-releasing capacity of the C(2)-substituent is increased. It is well established [2] that a ferrocenyl group can stabilise a carbonium-ion centre to a remarkable degree and, with this in mind, the properties of the 2-ferrocenylnorbornan-2-yl cation (I; R = Fc) have been studied. It was hoped that the resulting stability conferred upon the species might permit its isolation as a stable salt [3] whose structure could be thoroughly investigated, *e.g.* by crystallographic techniques.



(I)



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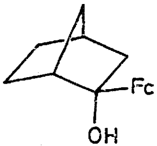

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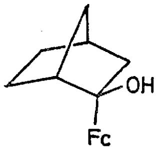

(IV)

The methods of preparation of the required precursors,* (II), (III), and (IV) have been described [4] previously. Treatment of these compounds either with 90% HCO_2H aq. or under Bertram–Walbaum conditions [5] ($HOAc–H_2SO_4$ aq.) produced dark red solutions which, after hydrolysis, gave rise to identical product mixtures (Experimental section). After chromatographic separation, it was established that, irrespective of the starting material, the main product was the alkene (II) (*ca.* 63%) with smaller proportions of the *endo*-alcohol (III) (*ca.* 25%) and its epimer (IV) (*ca.* 10%). Clearly, the species common to these acidic solutions is the 2-ferrocenylnorbornan-2-yl cation (I; R = Fc), a conclusion which is supported by spectral measurements which are detailed later. The absence of products of Wagner–Meerwein rearrangement of this cation contrasts with the behaviour under similar conditions of the phenyl analogue (I; R = Ph) reported [6] by Kleinfelter and Schleyer. In this case, products derived only from a rearranged secondary carbonium ion were observed. However, the much greater disparity in thermodynamic stability between the corresponding 1- and 2-ferrocenylnorbornan-2-yl cations provides an unsurmountable energy barrier to the rearrangement even under strenuous equilibrating conditions.

An attempt to generate the cation (I; R = Fc) under aprotic conditions by hydride abstraction from 2-*endo*-ferrocenylnorbornane [4] with triphenylmethyl tetrafluoroborate was unsuccessful, tritylation of the ferrocene rings occurring.[7] However, this reagent quantitatively abstracted hydroxide ion from either of the alcohols (III) and (IV) in methylene chloride solution giving the cation (I; R = Fc) and triphenylmethanol. Repeated attempts to isolate and characterise the tetrafluoroborate salt present were unsuccessful. In each case, proton elimination occurred and the alkene (II) was formed. In order to circumvent this elimination, the preparation of a 3,3-disubstituted derivative of the cation was envisaged. However, with conditions [4] under which ferrocenyl-lithium adds smoothly to norbornan-2-one to give the alcohol precursor (III), no reaction was observed with its 3,3-dimethyl- or 1,3,3-trimethyl-derivatives (camphenilone and fenchone respectively). Presumably, the presence of the methyl groups close to the carbonyl group in these ketones introduces sufficient steric hindrance to prevent addition of a bulky nucleophile.

Hydrolysis of the cation (I; R = Fc) generated under these aprotic conditions again afforded a mixture of the alkene (II) (*ca.* 64%) and the epimeric alcohols (III) (*ca.* 8%) and (IV) (*ca.* 25%). The preponderance of the *exo*- over the *endo*-alcohol in this case (*cf.* product

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* For each of the formulae in the text, only one stereoisomeric form is depicted. All the compounds were racemic mixtures. Fc = ferrocenyl ($C_5H_5FeC_5H_4$) throughout.

[1] (*a*) J. A. Berson in 'Molecular Rearrangements,' Interscience, New York, 1963, part 1; S. Winstein in 'Organic Reaction Mechanisms,' *Chem. Soc. Spec. Publ.* No. 19, 1964; P. D. Bartlett, 'Non-Classical Ions,' Interscience, New York, 1965; G. D. Sargent, *Quart. Rev.*, 1966, **20**, 301; (*b*) H. C. Brown, *Chem. in Brit.*, 1966, 199; H. C. Brown, *Chem. Eng. News*, 1967, 87.

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

[3] *Cf.* M. Cais and A. Eisenstadt, *J. Org. Chem.*, 1965, **30**, 1148; A. N. Nesmeyanov, E. G. Perevalova, L. I. Leonteva, and O. F. Filippov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1967, 464, and earlier papers.

[4] M. J. A. Habib and W. E. Watts, *J. Chem. Soc.* (*C*), 1969, 1469.

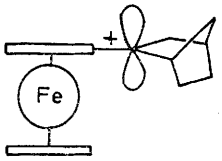
[5] J. Bertram and H. Walbaum, *J. prakt. Chem.*, 1894, **49**, 1.

[6] D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, 1961, **26**, 3740.

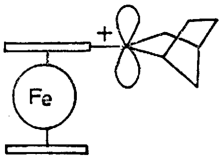
[7] M. J. A. Habib and W. E. Watts, unpublished research.

distribution from acidic media) may be attributed to kinetic factors. Since product formation under non-acidic conditions is irreversible, a greater proportion of the thermodynamically less-stable epimer (IV) results whereas, under equilibrating conditions, the more stable epimer (III) predominates.

These experiments show that the cation (I; R = Fc) undergoes proton elimination in preference to combination with a nucleophile. This may be attributed to a combination of steric and electronic factors. In the transition state for nucleophilic capture, the bulky ferrocenyl group is pushed towards either the C(7)-methylene group (*endo*-attack) or the C(5)–C(6)-ethylene bridge (*exo*-attack) imposing nonbonded interactions which effectively increase the energy requirements for these processes. Further, the gain in resonance energy associated with formation of a ferrocenylvinyl system, which possesses greater intrinsic thermodynamic stability than a styryl group,[8] would favour proton loss from the cation. Similar results have been reported[9] by Deno *et al.* who found that the major product formed upon acid treatment of 2-*exo*-*p*-methoxyphenylnorbornan-2-ol was the corresponding alkene derived from the intermediate cation (I; R = *p*-$MeOC_6H_4$) by proton loss.



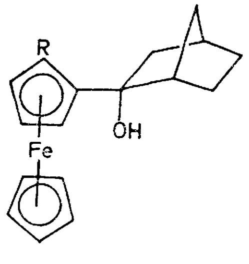
(V)



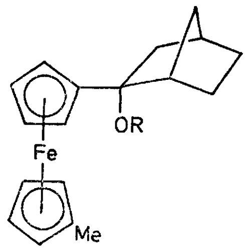
(VI)

The observation that both the *exo*- (IV) and *endo*-alcohol (III) are formed from the cation (I; R = Fc) *under kinetically controlled conditions* (aprotic media) is surprising since previous evidence suggests[1] that capture of a norbornan-2-yl cation by a nucleophile proceeds exclusively from the *exo*-direction. However, there are two discrete conformations of the cation [(V) and (VI)] which allow full conjugative overlap between the empty *p*-orbital at C(2) and the cyclopentadienyl ring π-orbitals. These should have different ground-state energies and would be present in unequal populations. It is also known from other studies[10] that the reaction of ferrocenylcarbonium ions with nucleophiles proceeds with high specificity from the side of the ligand remote from the iron atom. Consequently, if the normal steric control exerted by the norbornanyl framework is overruled by the space requirements of the ferrocenyl substituent, the cation in conformation (VI) would collapse to give the *endo*-alcohol (III), the epimer (IV) deriving from the alternative conformation (V).

In order to have available for spectral analysis (*vide infra*) methylferrocenyl analogues of the cation (I; R = Fc), the preparation of the related alcohols (VII; R = Me) and (VIII; R = H) was carried out as follows. The α-lithio-derivative[11] of *NN*-dimethylaminomethylferrocene ($FcCH_2NMe_2$) was condensed with norbornan-2-one to give, after hydrolysis, an amino-alcohol (VII; R = CH_2NMe_2) whose structure is assigned on the basis of the established[4] *exo*-mode of additions to the carbonyl group in this ketone. Sodium amalgam reduction of the methiodide salt (VII; R = $CH_2\overset{+}{N}Me_3I^-$) of this amine in aqueous tetrahydrofuran afforded a low yield of the α-methyl derivative (VII; R = Me) together with the diol (VII; R = CH_2OH), the major product. This diol was also formed when a similar reduction was attempted in aqueous ethanol. The major product from this reaction proved to be the ether (VII; R = CH_2OEt) and no α-methyl compound was isolated.



(VII)



(VIII)

The 1′-methyl isomer (VIII; R = H) was obtained by treatment of the alcohol (III) with n-butyl-lithium followed by iodomethane. Predictably, the corresponding ether (VIII; R = Me) was also isolated and the 1,1′-disposition of the ferrocenyl substituents in these products was established by the absence in their i.r. spectra of bands diagnostic[12] of an unsubstituted cyclopentadienyl ring. Although earlier work[13] has led to the conclusion that metallation of hydroxyalkylferrocenes of the type ($FcCR_2OH$) occurs preferentially at ring positions adjacent to the substituent, the absence in the above reaction of products derived from such an intermediate may be due to the steric hindrance to α-lithiation introduced by the bulky norbornanyl substituent.

^1H *N.m.r. Spectra*.—The ^1H n.m.r. spectra of the alkene (II) and the alcohols (III) and (IV) in trifluoroacetic acid are identical and distinct from those determined in deuteriochloroform (Table 1). The absence in this spectrum of low-field signals attributable to protons directly bonded to a carbonium-ion centre rules out the possibility of the presence of ions resulting from Wagner–Meerwein or hydride-shift rearrangement and the species common to these solutions is the classical 2-ferrocenylnorbornan-2-yl cation (I; R = Fc).

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[8] M. J. A. Habib, J. Park, and W. E. Watts, *J. Organometallic Chem.*, 1970, **21**, P. 59.

[9] N. C. Deno, P. von R. Schleyer, and D. C. Kleinfelter, *Tetrahedron Letters*, 1961, 414.

[10] *E.g.*, see D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, 1960, No. 13, 1.

[11] D. W. Slocum, B. W. Rockett, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1965, **87**, 1241; E. S. Bolton, P. L. Pauson, M. A. Sandhu, and W. E. Watts, *J. Chem. Soc.* (*C*), 1969, 2260.

[12] M. Rosenblum, *Chem. and Ind.*, 1958, 953.

[13] R. A. Benkeser, W. P. Fitzgerald, and M. S. Meltzer, *J. Org. Chem.*, 1961, **26**, 2569.

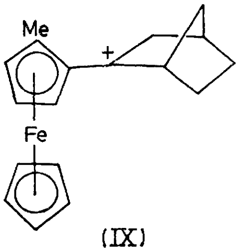
TABLE 1

^{1}H N.m.r. spectra of the 2-ferrocenylnorbornan-2-yl and related cations [a,b]

Compound	Solvent	Species present	Cyclopentadienyl protons (τ) H_α	H_β	$H_{\text{remainder}}$	Methyl protons [c] (τ)	Norbornanyl protons (τ)	Hydroxyl protons [d] (τ)
(II)	$CDCl_3$	(II)	5·6—5·9	5·6—5·9	5·92 [c]		6·8—9·0 [e]	
(III) or (IV)	$CDCl_3$	(III) or (IV)	5·8—5·9	5·8—5·9	5·82 [c]		7·5—9·0	7·74 (III) 7·56 (IV)
(II), (III), or (IV)	CF_3CO_2H	(I; R = Fc)	4·9—5·1	3·5—3·8	5·03 [c]		6·6—8·7	
(VII; R = Me)	$CDCl_3$	(VII; R = Me)	5·7—6·0	5·7—6·0	5·86 [c]	7·96	7·4—8·8	7·63
(VII; R = Me)	CF_3CO_2H	(IX)	5·1—5·4	3·8—3·95	5·16 [c]	7·98	6·2—8·8	
(VIII; R = H)	$CDCl_3$	(VIII; R = H)	5·7—6·1	5·7—6·1	5·92 [c]	8·02	7·6—8·9	7·70
(VIII; R = H)	CF_3CO_2H	(X)	5·0—5·4	3·7—3·95	5·0—5·4	8·22	6·6—9·0	

[a] At 40 MHz using tetramethylsilane as internal reference. [b] All the resonances were multiplets unless indicated otherwise; integrated relative intensities were in accord with the assignments. [c] Singlet resonance. [d] Broadened singlet resonance. [e] Vinyl proton appears at τ 4·1br(d).

Previous work[14] has led to the conclusion that ring protons located β- to the positively charged substituent in ferrocenylcarbonium ions resonate at lower field than the corresponding α-protons. This effect is illustrated by comparison of the spectra (Table 1) of the parent (I; R = Fc) and the methyl-substituted cations (IX) and (X). In each of these spectra, the multiplet appearing at lowest field (around τ 3·8) integrated for two protons corresponding to the β-protons of the ring bearing the positively charged substituent. The resonance of the α-proton(s) of this ring and of the protons of the other cyclopentadienyl ring overlap (around τ 5·1) giving rise to a 7-proton multiplet for the parent cation (I; R = Fc) and to 6-proton multiplets for the methyl-substituted derivatives (IX) and (X).



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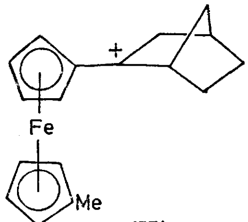


(X)

Electronic Spectra.—Solutions of either the alkene (II) or the alcohols (III) and (IV) in acidic media give rise to identical electronic spectra which are relatively insensitive to the nature of the medium and therefore represent the 2-ferrocenylnorbornan-2-yl cation (I; R = Fc) (Table 2). Similarly, the 1′-methyl analogue (X) is formed from either the alcohol (VIII; R = H) or the ether (VIII; R = Me) in acidic solutions. In 50% H_2SO_4 aq., the spectrum of the cation (I; R = Fc) contains a strong absorption band centred at 264 nm. which is absent in the spectra of the precursors and most probably represents a $\pi \longrightarrow \pi^*$ transition associated with the cationic ligand. Similarly, Hill and Wiesner found[15] that, in H_2SO_4 aq., the ferrocenylmethyl cation ($FcCH_2^+$) gives rise to an absorption maximum at 256 nm. and reported that the spectrum was unchanged with acid concentrations up to 96%.

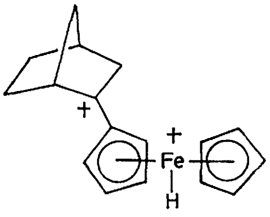
The spectrum of the cation (I; R = Fc), however, changes with sulphuric acid concentration and a new absorption band, whose intensity increases slowly with time, appears around 378 nm. in solutions of acid concentration greater than 80%. Upon dilution of these solutions, the spectrum previously observed in 50% acid is regenerated. These results indicate that the first-formed cation (I; R = Fc) is slowly converted into a new species in media of high acidity. Since the reaction

TABLE 2

Electronic spectra of the 2-ferrocenylnorbornan-2-yl and related cations

Precursor	Cation	Solvent	Absorption maxima [a] nm. (log ε)	
(II), (III), or (IV)	(I; R = Fc)	*b*	267 (4·14)	
		c	267 (4·12)	
		d	264 (4·02)	
	(I; R = Fc) + (XI)	*e*	258 (3·99)	378 (4·06) [f]
(VIII; R = H or Me)	(X)	*d*	269 (4·10)	
$FcCMe_2OH$	$\mathrm{Fc}\overset{+}{\mathrm{C}}\mathrm{Me}_2$	*b*	263 (4·05) [f]	
		d	261 (4·09)	
	$\mathrm{Fc}\overset{+}{\mathrm{C}}\mathrm{Me}_2$ + Fe-protonated species	*e*	259 (4·02)	362 (3·95) [f]

[a] Spectra also contain unresolved absorptions appearing as shoulders or inflections in the 280—370 nm. region and a broad band in the visible region at *ca*. 455 nm. (log ε 3·10—3·15). [b] Conc. HCl. [c] Glacial HOAc containing a trace of conc. H_2SO_4. [d] 50% (v/v) H_2SO_4 aq. [e] 80% (v/v) H_2SO_4 aq. [f] Time-sensitive absorption; values given for freshly prepared solutions.



(XI)

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[14] 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; J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, 1969, **91**, 4324.

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

is reversible it is unlikely that skeletal or hydride-shift rearrangement is occurring. The most plausible interpretation is that, in strong acid, the cation (I; R = Fc) undergoes slow and reversible protonation on the iron atom producing a dication (XI). Previous work has shown[16] that ferrocene itself may be similarly protonated by co-ordination of a proton to a pair of non-bonding electrons located on the metal atom.

This behaviour appears to be characteristic of tertiary ferrocenylalkyl cations ($Fc\overset{+}{C}R_2$). For example, the 2-ferrocenylpropan-2-yl cation absorbs strongly at 261 nm. in 50% H_2SO_4 aq. and at 259 and 362 nm. in 80% acid (Table 2). In the case of the secondary ferrocenylalkyl cations ($Fc\overset{+}{C}HR$) and the ferrocenylmethyl cation[15] itself, the greater electron-withdrawing power of the C^+ substituent effectively reduces the basicity of the iron atom and protonation under similar conditions is not observed.[7]

EXPERIMENTAL

All reactions were carried out under purified nitrogen. Yields of product are based upon starting material consumed. M.p.s were measured for samples in sealed evacuated capillaries. Chromatography was carried out with Spence Grade H alumina, partially deactivated by exposure to the atmosphere. Light petroleum refers to the fraction of b.p. 40—60°. ^{1}H N.m.r. spectra were recorded with a Perkin-Elmer R10 spectrometer at 40 MHz for deuteriochloroform solutions unless stated otherwise with tetramethylsilane as internal reference; i.r. spectra were obtained with a Perkin-Elmer 137 spectrometer; electronic spectra were obtained with a Unicam SP 800A spectrometer, calibrated against holmium film. Molecular weights were determined by accurate mass measurement of the ^{56}Fe molecular ion in the mass spectra, which were obtained with an A.E.I. MS9 spectrometer at 70 eV.

2-(NN-*Dimethylaminomethyl*)-1-(2-endo-*hydroxynorbornan-2-ylferrocene* (VII; R = CH_2NMe_2).—A solution of *NN*-dimethylaminomethylferrocene[17] (12·5 g., 0·05 mole) in dry tetrahydrofuran (100 ml.) was mixed with a solution of n-butyl-lithium (4·6 g., 0·07 mole) in ether–hexane (1 : 1; 65 ml.) and the mixture was stirred for 4 hr. A solution of norbornan-2-one[6] (8·0 g., 0·07 mole) in dry ether (30 ml.) was added slowly. The mixture was stirred overnight and then diluted with water (600 ml.); the organic layer was separated and combined with two benzene extracts of the aqueous layer. The total extract was washed with water, dried (Na_2SO_4), and evaporated, and the residue was dissolved in benzene and chromatographed on alumina. Light petroleum eluted the *amino-alcohol* (VII; R = CH_2NMe_2) (6·0 g., 55%), which crystallised from light petroleum as a yellow solid, m.p. 110—112° (Found: C, 67·8; H, 7·7%; *M*, 353·1449. $C_{20}H_{27}FeNO$ requires C, 68·0; H, 7·7%; *M*. 353·1442), $\nu_{max.}$ (KCl) 3260 cm.$^{-1}$ (OH); τ 5·8—6·3 (10H. m, ferrocenyl and CH_2), 7·48 (6H, s, Me), and 7·1—8·9 (11H, m, remainder). Light petroleum–ether (2 : 1) eluted unchanged amine (5·0 g., 40% recovery).

The *methiodide* (VII; R = $CH_2\overset{+}{N}Me_3I^-$) was prepared by treatment of the above amino-alcohol in benzene solution with an excess of iodomethane, m.p. 60° (decomp.) (Found: C, 51·2; H, 6·2. $C_{21}H_{30}FeINO$ requires C, 50·9; H, 6·1%), $\nu_{max.}$ (KCl) 3460 cm.$^{-1}$ (OH).

Sodium Amalgam Reduction of the Methiodide (VII; R = $CH_2\overset{+}{N}Me_3I^-$).—(*a*) A solution of the methiodide (1·0 g., 2 mmole) in water–tetrahydrofuran (3 : 1; 200 ml.) was added to sodium amalgam (3%; 70 g., 0·9 g.-atom Na) and the mixture was heated under reflux until all of the amalgam had reacted. The solution was decanted from the residual mercury and extracted thoroughly with ether. The extract was dried (Na_2SO_4) and evaporated, and the residue was dissolved in benzene and chromatographed on alumina. Light petroleum eluted 1-(2-endo-*hydroxynorbornan*-2-*yl*)-2-*methylferrocene* (VII; R = Me) (0·15 g., 24%) which gave yellow needles, m.p. 97—98° (from light petroleum) (Found: C, 69·4; H, 7·4%; *M*, 310·1032. $C_{18}H_{22}FeO$ requires C, 69·7; H, 7·1%; *M*, 310·1020), $\nu_{max.}$ (KCl) 3560 cm.$^{-1}$ (OH). Light petroleum–ether (1 : 1) eluted 1-(2-endo-*hydroxynorbornan*-2-*yl*)-2-(*hydroxymethyl*)*ferrocene* (VII; R = CH_2OH) (0·45 g., 68%) which gave fine yellow crystals, m.p. 84—85° (from light petroleum–ether) (Found: C, 66·1; H, 6·7; O, 9·7%; *M*, 326·0980. $C_{18}H_{22}FeO_2$ requires C, 66·3; H, 6·8; O, 9·8%; *M*, 326·0970), $\nu_{max.}$ (KCl) 3270 cm.$^{-1}$ (OH); τ 5·6 (2H, s, CH_2), 5·82 and 5·92 (8H, 2 s, ferrocenyl), 6·8br (2H, s, OH), and 7·6—9·1 (10H, m, norbornanyl).

(*b*) A solution of the methiodide (1·5 g., 3 mmole) in aqueous ethanol (1 : 1; 100 ml.) was treated with sodium amalgam (3%; 80 g., 1·05 g.-atom Na) as described in the preceding experiment and the product was dissolved in light petroleum and chromatographed on alumina. Light petroleum eluted 1-(2-endo-*hydroxynorbornan*-2-*yl*)-2-(*ethoxymethyl*)*ferrocene* (VII; R = CH_2OEt) (0·8 g., 73%) which distilled at 170°/0·01 mm. as a yellow oil (Found: C, 68·2; H, 7·4%; *M*, 354·1290. $C_{20}H_{26}FeO_2$ requires C, 67·8; H, 7·3%; *M*, 354·1282), $\nu_{max.}$ (LF) 3450 cm.$^{-1}$ (OH); τ 5·8 (8H, s, ferrocenyl), 5·9 (2H, s, CH_2), 6·4 (2H, q, CH_2), 7·6—8·7 (10H, m, norbornanyl), 8·26 (1H, s, OH), and 8·78 (3H, t, Me). Light petroleum–ether (1 : 1) eluted a product (0·23 g., 23%) which was identical with the diol (VII; R = CH_2OH) described under (*a*); m.p. and mixed m.p. 84—85°.

1-(2-endo-*Hydroxynorbornan*-2-*yl*)-1′-*methylferrocene* (VIII; R = H).—A solution of n-butyl-lithium (1·6 g., 0·025 mole) in ether–hexane (1 : 1; 22 ml.) was added to a solution of 2-*exo*-ferrocenylnorbornan-2-ol[4] (3·0 g., 0·01 mole) in ether (50 ml.) and the mixture was stirred overnight. Iodomethane (142 g., 1·0 mole) in ether (50 ml.) was added and the mixture was heated under reflux for 8 hr. Water (300 ml.) was added and the organic layer was separated and combined with two ether extracts of the aqueous layer. The total extract was washed with water, dried (Na_2SO_4), and evaporated, and the residue was dissolved in light petroleum and chromatographed on alumina. Light petroleum eluted 1-(2-endo-*methoxynorbornan*-2-*yl*)-1′-*methylferrocene* (VIII; R = Me) (1·78 g., 56%) which distilled at 165°/0·1 mm. as a yellow oil (Found: C, 70·0; H, 7·5%; *M*, 324·1184. $C_{19}H_{24}FeO$ requires C, 70·4; H, 7·4%; *M*, 324·1180), $\nu_{max.}$ (LF) 1080 cm.$^{-1}$ (OMe); τ 5·7—6·1 (8H, m, ferrocenyl), 7·22 (3H, s, OMe), 8·03 (3H, s, Me), and 7·4—8·8 (10H, m, norbornanyl). Light

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petroleum–ether (9 : 1) eluted the *alcohol* (VIII; R = H) (0·9 g., 31%) which distilled at 150°/0·05 mm. as a dark yellow oil (Found: C, 69·3; H, 7·1%; *M*, 310·1020. $C_{18}H_{22}FeO$ requires C, 69·7; H, 7·1%; *M*, 310·1020), $\nu_{max.}$ (LF) 3565 cm^{-1} (OH); light petroleum–ether (3 : 2) eluted unchanged alcohol (0·2 g., 7% recovery).

Reactions involving the 2-*Ferrocenylnorbornan*-2-*yl Cation* (I; R = Fc).—(*a*) On addition of 2-ferrocenylnorborn-2-ene[4] (1·7 g., 6 mmole) to formic acid (90% v/v; 50 ml.), an immediate dark red colour developed. The solution was stirred overnight, then poured into water (250 ml.), and extracted thoroughly with ether. The extract was washed (Na_2CO_3 aq.), dried (Na_2SO_4), and evaporated, and the residue was dissolved in light petroleum and chromatographed. Light petroleum eluted the alkene (II) (1·07 g., 63%), identical with the starting material. Light petroleum–ether (3 : 2) eluted the *endo*-alcohol (III) (0·45 g., 25%) followed by the *exo*-alcohol (IV) (0·18 g., 10%), both identical with authentic specimens.[4]

Almost identical product mixtures were obtained using either of these alcohols as starting material in the reaction.

(*b*) Aqueous sulphuric acid (50% v/v; 2 ml.) was added to a solution of the alkene (II) (1·7 g., 6 mmole) in glacial acetic acid (50 ml.). A dark red solution was immediately formed. The solution was poured into water (250 ml.) and extracted thoroughly with ether. The extract was washed (Na_2CO_3 aq.), dried (Na_2SO_4), and evaporated, and the residue was separated as in the previous experiment affording the alkene (II) (1·09 g., 64%), the *endo*-alcohol (III) (0·43 g., 24%), and the *exo*-alcohol (IV) (0·16 g., 9%).

Similar results were obtained using either of these alcohols as starting material in the reaction.

(*c*) A solution of the alcohol (III) (1·8 g., 6 mmole) in methylene chloride (50 ml.) was added to a solution of triphenylmethyl tetrafluoroborate[18] (2·3 g., 7 mmole) in methylene chloride (50 ml.), an immediate dark red solution being formed. The solution was stirred overnight and then stirred with saturated sodium hydrogen carbonate solution, the colour reverting to orange-yellow. The organic layer was separated and combined with two methylene chloride extracts of the aqueous layer. The total extract was washed (H_2O), dried (Na_2CO_3), and evaporated. The residue was triturated with a little light petroleum giving a white precipitate of triphenylmethanol (1·42 g., 78%), m.p. 162—163°, identical with an authentic specimen. The precipitate was filtered off and the filtrate was chromatographed as in the previous experiments. There was obtained the alkene (II) (1·09 g., 64%), the *endo*-alcohol (III) (0·14 g., 8%), and the *exo*-alcohol (IV) (0·45 g., 25%).

An almost identical product mixture was obtained using the *exo*-alcohol (IV) as starting material in the reaction.

Attempted Preparation of 2-*Ferrocenylnorbornan*-2-*yl Tetrafluoroborate*.—A solution containing equimolar amounts of the *endo*-alcohol (III) and triphenylmethyl tetrafluoroborate in methylene chloride was diluted with light petroleum. A gummy solid formed which could not be crystallised. The solution was evaporated to dryness and the residual gum was extracted with hot light petroleum affording the alkene (II).

Further attempts to isolate a salt from the above solution using different solvents were unsuccessful.

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