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BRIDGED FERROCENES—XI[1]

THE ^{1}H NMR SPECTRA OF [3](1,2)FERROCENOPHANE DERIVATIVES AND THE DIAMAGNETIC ANISOTROPY OF THE FERROCENE MOLECULE

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Abstract—The ^{1}H NMR spectra of a series of homoannularly bridged [3](1,2)ferrocenophane derivatives have been recorded. Comparison of the spectra of epimeric compounds in this series has established that the protons of an *exo* substituent (*i.e.* located above the plane of the cyclopentadienyl ring remote from the iron atom) are shielded compared with the protons of the same substituent in an *endo* configuration (*i.e.* below the plane of the cyclopentadienyl ring). The region close to the iron atom is strongly shielding in nature.

INTRODUCTION

IN AN ATTEMPT TO CLARIFY the nature of the ring-metal bonding forces in ferrocene, Mulay and Fox determined the principal magnetic susceptibilities of the molecule.[2] They found that the susceptibility along the molecular axis perpendicular to the planes of the cyclopentadienyl rings and passing through their centre of mass was much greater than those along the axes in the plane containing the iron atom parallel to the planes of the rings ($\Delta K = 49{\cdot}5 \times 10^{-6}$ cgs units). This result was interpreted in favour of an electronic structure in which there is considerable π-electron circulation associated with each cyclopentadienyl ring. In consequence, when the molecule is exposed to an applied magnetic field, the π-electron ring currents thereby induced create a local diamagnetic field around the molecule.

As in the case of carbo- and hetero-cyclic aromatic compounds, the presence of this induced field leads to the existence of shielding and deshielding regions around the molecule which can be probed by ^{1}H NMR spectroscopy. By analogy with these other aromatic systems, it would be expected that protons located in the volume above the plane of the cyclopentadienyl ring opposite from the iron atom would experience a shielding effect since the induced diamagnetic field acts to oppose the applied magnetic field in this region. Protons held in the volume between the planes of the rings, on the other hand, would be located in a deshielding zone. However, since the region close to the iron atom is high in electron density (three essentially nonbonding electron pairs fill the metal a_{1g} and e_{2g} levels[3]), protons held in close proximity to the iron atom should be strongly shielded. This reasoning leads to a picture of the shielding (+) and deshielding (−) regions around the ferrocene molecule as depicted in the Figure.

Although ^{1}H NMR spectroscopy has proved particularly useful and has been used extensively in the investigation of the organic chemistry of ferrocene and its derivatives,[4] little information bearing upon the diamagnetic anisotropy of the system

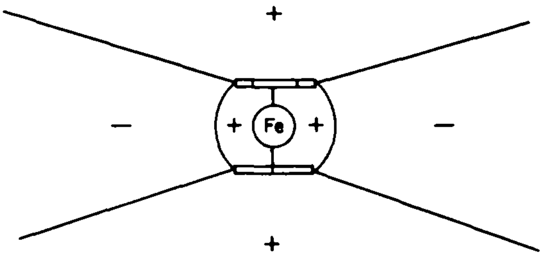
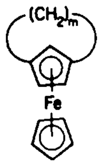
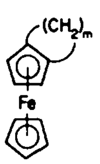


FIG. Shielding (+) and deshielding (−) regions around the ferrocene molecule

has been forthcoming and no serious attempt to map the shielding and deshielding regions associated with the ferrocene molecule has been reported. The few relevant ^{1}H NMR spectra which have been described have been interpreted both in support[5] and in disagreement[6] with the picture (Figure) based upon the susceptibility measurements[2] of Mulay and Fox.

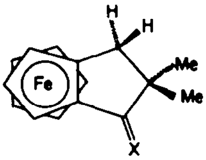


I



II

Our first approach to this problem centred upon attempts to prepare homoannularly bridged [m] (1,3)ferrocenophanes (I; $m > 7$) in which the hydrocarbon chain would be sterically constrained to pass over the top of the cyclopentadienyl ring. A similar approach has previously been used successfully to explore the diamagnetic anisotropy of the benzene molecule.[7] Since our synthetic attempts in this direction have so far been frustrated,[8] we turned our attention to the more accessible [m](1,2)ferrocenophane systems (II) in which adjacent positions of a cyclopentadienyl ring are bridged by a hydrocarbon chain. The substituent atoms or groups attached to the carbon bridge in compounds of this type may be connected either in an *exo* (*i.e.* directed away from the iron atom) or an *endo* configuration (*i.e.* directed towards the iron atom) and it was hoped that analysis of the ^{1}H NMR spectra of a range of suitably substituted compounds would provide information regarding the diamagnetic anisotropy of the ferrocene molecule. In order to minimise complications arising from puckering and conformational flexing of the alicyclic ring, the [3](1,2)-ferrocenophane system (II; $m = 3$) was selected as the most suitable for this study. The three-carbon bridge in this molecular framework is constrained to lie approximately in the plane of the cyclopentadienyl ring to which it is attached and its conformational flexibility is severely restricted.



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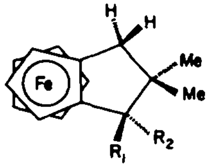
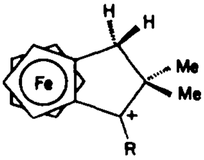


IV



V

TABLE. ^{1}H NMR SPECTRA OF [3](1,2)FERROCENOPHANE DERIVATIVES[a]

No.	Compound	Me$_2$C Resonances[b]			H$_2$C Resonances[c]			R$_1$ Resonances[d]	R$_2$ Resonances[d]	X Resonances[d]	Cyclopentadienyl Resonances[e]
	Formulae	τ_{exo}	τ_{endo}	$\Delta\tau$	τ_{exo}	τ_{endo}	$\Delta\tau$	τ_{exo}	τ_{endo}	τ	τ
1	III: X = O	8·90	8·57	0·33	7·46	7·12	0·34	—	—	—	5·87 (s): 5·3–5·6 (m)
2	III: X = CH$_2$	8·88	8·53	0·35	7·62	7·27	0·35	—	—	4·90, 5·13 (2 bs)	6·01 (s): 5·68 (t): 5·85 (m)
3	IV: R$_1$ = Me, R$_2$ = OH	9·18[f]	8·71[f]	0·47	8·04	7·29	0·75	8·75 (s: Me)[f]	7·55 (s: OH)	—	5·84 (s): 5·9–6·1 (m)
4	IV; R$_1$ = R$_2$ = H	8·94	8·60	0·34	7·82	7·45	0·37	7·82 (d: H)	7·45 (d: H)	—	5·97 (s): 6·0–6·1 (m)
5	IV; R$_1$ = H, R$_2$ = D	8·94	8·60	0·34	7·82	7·45	0·37	7·82 (H)[g]	—		5·97 (s): 6·0–6·1 (m)
6	IV: R$_1$ = D, R$_2$ = H	8·94	8·60	0·34	7·82	7·45	0·37	—	7·45 (H)[g]	—	5·97 (s): 6·0–6·1 (m)
7	IV: R$_1$ = Me, R$_2$ = H	9·20	8·70	0·50	6·8–8·0 (m)[h]		—	9·05 (d: Me)	6·8–8·0 (H)[h]	—	6·01 (s): 6·0–6·2 (m)
8	IV: R$_1$ = H, R$_2$ = Me	8·96	8·70	0·26	7·7–8·0 (m)[h]		—	7·7–8·0 (H)[h]	8·79 (d: Me)	—	5·90 (s): 5·9–6·3 (m)
9	IV: R$_1$ = H, R$_2$ = OH	9·00	8·72	0·28	7·90	7·45	0·45	5·95 (s: H)	8·00 (s: OH)	—	5·81 (s): 5·9–6·1 (m)
10	IV; R$_1$ = OH, R$_2$ = H	8·99	8·55	0·44	7·72	7·49	0·23	5·2 (bs: OH)	5·7–6·0 (H)[i]	—	5·96 (s): 5·7–6·0 (m)
11	IV: R$_1$ = H, R$_2$ = OMe	8·96	8·71	0·25	7·91	7·43	0·48	6·24 (s: H)	6·50 (s: OMe)	—	5·83 (s): 5·9:6·1 (m)
12	IV; R$_1$ = OMe, R$_2$ = H	8·98	8·52	0·46	7·74	7·53	0·21	6·62 (s: OMe)	5·63 (s: H)	—	5·95 (s): 5·8–6·0 (m)

[a] In CDCl$_3$ solution; TMS internal standard

[b] Two equally intense singlets

[c] AB pattern; $J_{AB} \sim 16$ Hz

[d] See formulae III and IV; signal multiplicity is indicated in brackets; (s) singlet, (bs) broadened singlet, (d) doublet

[e] Singlet resonance for the protons of the unsubstituted ring

[f] Tentative assignment

[g] Poorly resolved triplet (H/D coupling)

[h] Resonances of the methylene and methine protons overlap in this region

[i] Methine proton resonance lies under the cyclopentadienyl resonances

Synthetic methods

The compounds prepared in this investigation are listed in the Table. The starting material chosen for their preparation was the ketone III (X = 0; *i.e.* compound **1**) which was obtained by the method described by Rosenblum *et al.*[9] The stereochemistry assigned to these compounds rests on firm grounds. It is well established[5b, 10] that addition of a reagent to an unsaturated carbon atom (*e.g.* carbonyl, vinylic, or cationic) attached directly to a ferrocene ring occurs predominantly if not exclusively from the *exo* direction.* Thus, the alcohols (**3** and **9**), formed as the sole products of nucleophilic addition of methanide (from MeLi) and hydride (from LAH) respectively to the ketone (**1**), must contain an *endo* hydroxyl group. This assignment was confirmed by the presence in the IR spectra of these alcohols of a strong intramolecular Fe-bonded† hydroxyl stretching absorption[10b, 14] around 3550 cm^{-1}.

Similarly, the *exo* methyl structure (**7**) may be confidently assigned to the product of addition of methanide (from MeLi) to the stable carbonium ion V (R = H), generated by hydroxide abstraction[15] from the alcohol (**9**) using triphenylmethyl tetrafluoroborate. The corresponding *endo* methyl epimer (**8**) was obtained both by addition of hydride (from LAH) to the carbonium ion V (R = Me), generated by hydroxide abstraction from the alcohol (**3**), and by catalytic hydrogenation of the alkene (**2**). The last compound was prepared by dehydration of the alcohol (**3**). These methyl epimers (**7** and **8**) have distinctive spectroscopic properties (see Table).

The *exo* alcohol (**10**) was obtained by treatment of its epimer (**9**) with aqueous acid whereupon an equilibrium mixture of both alcohols was formed. This mixture, in which the *endo* alcohol (**9**) slightly predominated (*ca.* 60%), was readily separated by chromatography on alumina. The IR spectrum of the *exo* alcohol (**10**) lacked the low frequency hydroxyl stretching absorption found in the spectrum of its epimer (**9**). When this equilibration reaction was conducted in acidified MeOH solution, a readily separable mixture of the epimeric ethers (**11** and **12**) was formed in which the *exo*-ether (**12**) predominated (*ca.* 60%). The structures of these compounds were assigned from comparison of their ^1H NMR spectra (see Table) with those of the corresponding alcohols (**9** and **10**). In particular, the cyclopentadienyl proton patterns in these spectra are characteristic of the configuration of the oxygen atom attached either *exo* or *endo* to the bridging three-carbon chain.

Mixed-hydride reduction (LAH/$AlCl_3$) of the *endo* alcohol (**3**) was found to give exclusively the *endo* methyl derivative (**8**) whose structure had previously been established (*vide supra*). This reaction therefore proceeds with inversion of configuration at the reduction site.‡ The mechanism of the process probably involves abstraction of the hydroxyl group from the alcohol by the trivalent aluminium Lewis acid present in the reaction medium. Concerted or consecutive *exo* addition of hydride to the

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* A similar preference for *exo* addition to the ligand is shown in the reactions of other hydrocarbon-transition metal complexes.[11] This situation may reflect steric-approach control of product formation although electronic factors may also be important.[11, 12]

† The assignment of such absorption bands as Fe-bonded frequencies has been questioned by Traylor who has alternatively suggested that interaction between the hydroxyl group and the interannular bonding electrons may account for the low frequency of the absorption.[13]

‡ Related reactions which lead to retention of configuration at the reduction site have also been reported.[16]

developing or fully developed carbonium-ion centre would then lead to a product of inverted configuration, as found experimentally.

By direct analogy, the *exo* deuterio structure (**6**) is assigned to the product of mixed-deuteride reduction (LAD/$AlCl_3$) of the secondary *endo* alcohol (**9**). In harmony with the carbonium-ion mechanism suggested for these reductions (*vide supra*), it was found that the same product (**6**) (identical IR and ^1H NMR spectra) was formed upon mixed-deuteride reduction of the epimeric *exo* alcohol (**10**). Hydroxide abstraction from either epimer (**9** or **10**) would afford the same carbonium ion (V; R = H) leading to the product (**6**) by *exo* addition of deuteride. Using a similar approach, the corresponding *endo* deuterio compound (**5**) was prepared by mixed-hydride reduction of the alcohol IV (R_1 = D, R_2 = OH), the product of LAD reduction of the ketone (**1**) (*cf.* preparation of **9**). The all-proton analogue (**4**) of these selectively deuteriated compounds was simply obtained by mixed-hydride reduction of the parent ketone (**1**).

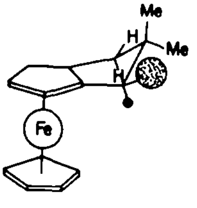
DISCUSSION

Details of the ^1H NMR spectra ($CDCl_3$ solutions) of the compounds prepared are given in the Table. These spectra illustrate clearly the differential shielding experienced by atoms or groups depending upon their attachment to the bridge in either an *exo* or an *endo* configuration. Thus, a chemical-shift difference of 0·34–0·37 ppm is found between the protons of the methylene group(s) in the ketone (**1**), the alkene (**2**), and the saturated compound (**4**). For these same three derivatives, the two singlet resonances of the methyl groups attached to C_β are separated by a similar amount (0·33–0·35 ppm).

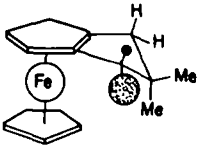
Comparison of the spectra of the compounds of the four epimeric pairs (**5–12**) establishes that, with the exception of the hydroxyl group (*vide infra*), the resonance of a C_α substituent occurs at higher field when the group is attached in the *exo* configuration. For example, the protons of an *exo* α-methyl group resonate at 0·26 ppm higher field than that found for the protons of an endo α-methyl group (*cf.* compounds **7** and **8**). For *exo* and *endo* α-methoxyl substituents (*cf.* compounds **11** and **12**), the corresponding chemical-shift difference is 0·12 ppm, the *exo* ether (**12**) giving the higher-field resonance, Similarly, the spectra of the selectively deuteriated compounds (**5** and **6**) show that it is the *exo* hydrogen atom of the α-methylene group which resonates at higher field. Since these results show clearly that the *exo* side of the alicyclic ring experiences greater shielding than the *endo* side at the α-carbon atom, it appears reasonable to assume that this situation would also extend to the β-carbon atom. The higher-field resonance of the Me_2C group in these compounds is accordingly assigned to the *exo* methyl group (Table).

The existence of a strongly hydrogen-bonded hydroxyl group in the *endo* alcohols (**3** and **9**) has already been mentioned. Since the chemical shifts of the hydroxyl protons in these alcohols appear at much higher field than the corresponding resonance of the *exo* alcohol (**10**), it may be concluded that the region close to the iron atom is strongly shielding in influence, in agreement with expectation (*vide supra*). This phenomenon has previously been commented upon by Rosenblum.[17]

Finally, the sensitivity of the methylene and Me_2C *exo–endo* chemical-shift differences (see $\Delta\tau$ values in Table) to structural factors merits comment. For those compounds in which two groups of disparate steric bulk are attached to the α-carbon atom (*i.e.* compounds **7–12**), a much larger separation between the two Me_2C signals is found for those compounds in which the bulkier α-substituent is attached in an *exo* configuration (*i.e.* compounds **7**, **10**, and **12**). The separation of the chemical shifts of the *exo* and *endo* methylene protons, on the other hand, is much larger for those compounds in which the bulkier group occupies an *endo* position (*i.e.* compounds **8**, **9**, and **11**).



VI



VII

For a stereochemistry in which the three-carbon bridge is coplanar with the cyclopentadienyl ring to which it is attached, serious eclipsing strain between a bulky α-substituent and an adjacent β-methyl group is introduced (*cf.* the conformation of butane in which the terminal methyl groups are eclipsed is estimated to be 4·4–6·1 kcal.mole^{-1} less stable than the conformation in which the methyl groups are anti to each other[18]). This eclipsing strain can be partially relieved by a deformation of the ring into an envelope conformation in which the β-carbon atom is slightly displaced towards or away from the iron atom. Deformations of this nature result in a relocation (relative to the ferrocene unit) of the atoms or groups attached to the three-carbon bridge with corresponding changes in chemical-shift values resulting.

Although further work is required in this connection, the ^1H NMR results can be accommodated if it is assumed that a bulky *exo* α-substituent causes a displacement of the β-carbon atom away from the iron atom (*cf.* VI) whereas a bulky *endo* α-substituent produces a displacement in the opposite direction (*cf.* VII). In each case, the α-substituent attains a favourable *pseudo*-equatorial configuration. For these two envelope conformations of the alicyclic ring, the steric relationship between both the Me_2C and H_2C groups and the ferrocene unit differs appreciably. The relative locations of the individual methyl groups and methylene protons in the diamagnetic field associated with the ferrocene system are correspondingly different for each conformation leading to the observed variations in the Δτ values (Table).

CONCLUSION

The results obtained in this study are in harmony with a picture of the shielding and deshielding regions around the ferrocene molecule (Figure) based upon the magnetic susceptibility measurements[2] of Mulay and Fox.

EXPERIMENTAL

For general remarks, see Part I.[19] ^1H NMR spectra were recorded for $CDCl_3$ solutions on a Perkin–Elmer R12A spectrometer at 60 MHz using TMS as internal reference. IR spectra were obtained on a Perkin–Elmer 457 grating spectrometer for dilute CCl_4 solutions.

1-exo-2,2-*Trimethyl*[3](1,2)*ferrocenophan*-1-*ol* (**3**). A soln of the ketone[9] (**1**) (268 mg: 1·0 mmole) in dry ether (20 ml) was added dropwise to a stirred soln of an excess of MeLi in dry ether (30 ml). The mixture was stirred for 1 hr at room temp and excess MeLi destroyed by addition of MeOH. The mixture was poured into water (50 ml) and the organic layer separated and combined with several ether extracts of the aqueous phase. The total extract was washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ether and chromatographed on Al_2O_3. Ligroin–ether (3:1) eluted a single yellow band which afforded the alcohol (**3**) (260 mg: 92%) as a yellow solid, m.p. 66–67°. (Found: C, 67·8: H, 7·0. $C_{16}H_{20}FeO$ requires: C, 67·6: H, 7·1%). IR 3545 cm^{-1} (OH).

1-endo-*Hydroxy*-2,2-*dimethyl*[3](1,2)*ferrocenophane* (**9**). A soln of the ketone[9] (**1**) (268 mg: 1·0 mmole) in dry ether (20 ml) was added dropwise to a stirred suspension of LAH (60 mg: 1·5 mmole) in dry ether (25 ml) and the mixture stirred for 1 hr. Excess hydride was destroyed by addition of EtOAc and the mixture poured into water (100 ml). The organic layer was separated and combined with ether extracts of the aqueous phase. The total extract was washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ether and chromatographed on Al_2O_3. Ligroin–ether (3:1) eluted a single yellow band which afforded the alcohol (**9**) (250 mg: 92%) as a yellow liquid. (Found: C, 66·6: H, 6·6. $C_{15}H_{18}FeO$ requires: C, 66·7: H, 6·7%). IR 3550 cm^{-1} (OH).

2,2-*Dimethyl*-1-*methylene*[3](1,2)*ferrocenophane* (**2**). The alcohol (**3**) (140 mg: 0·5 mmole) was dissolved in EtOH (50 ml) containing conc H_2SO_4 (5 drops). The soln was stirred for 15 min at room temp and poured into water (200 ml). The mixture was extracted thoroughly with ether and the ether extracts were washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted a single yellow band which afforded the alkene (**2**) (120 mg: 90%) as an orange liquid which decomposed on standing. Satisfactory analytical data were not obtained. IR 1630 cm^{-1} (C=C).

1-exo-2,2-*Trimethyl*[3](1,2)*ferrocenophane* (**7**). Triphenylmethyl tetrafluoroborate[20] (225 mg: 0·65 mmole) was added to a stirred soln of the alcohol (**9**) (135 mg: 0·5 mmole) in dry ether (20 ml). A brown ppte of the ferrocenylcarbonium ion tetrafluoroborate formed immediately. After 10 min, excess MeLi in dry ether was added. The ppte immediately dissolved giving a yellow soln. The excess of MeLi was destroyed (MeOH) and the mixture poured into water. The organic layer was separated, washed (H_2O), and extracted thoroughly with aqueous $FeCl_3$ soln. The $FeCl_3$aq extract was washed with ether and the ferricenium salts present reduced by addition of $TiCl_3$aq. The soln was extracted with ether and the extract washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted a single yellow band which afforded compound (**7**) (75 mg: 50%) as a yellow liquid. (Found: C, 71·4: H, 7·3. $C_{16}H_{20}Fe$ requires: C, 71·6: H, 7·5%).

1-endo-2,2-*Trimethyl*[3](1,2)*ferrocenophane* (**8**). (a) Triphenylmethyl tetrafluoroborate[20] (450 mg: 1·3 mmole) was added to a stirred soln of the alcohol (**3**) (284 mg: 1·0 mmole) in dry ether (20 ml). A brown ppte of the ferrocenylcarbonium ion tetrafluoroborate formed immediately. After 10 min, excess LAH was added. The ppte immediately dissolved giving a yellow soln. The mixture was worked up as in the preceding experiment and the product dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted a single yellow band which afforded compound **8** (250 mg: 90%) as a yellow liquid. (Found: C, 71·3: H, 7·3. $C_{16}H_{20}Fe$ requires: C, 71·6: H, 7·5%).

(b) A soln of the alkene (**2**) (50 mg: 0·2 mmole) in EtOH (20 ml) was stirred over PtO_2 (20 mg) under H_2. When uptake of H_2 had ceased, the soln was filtered, diluted with water (100 ml), and extracted thoroughly with ether. The ether extracts were washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted compound **8** (46 mg: 92%), identical with that described under (a).

(c) Mixed-hydride reagent was prepared by addition of LAH (60 mg: 1·5 mmole) and $AlCl_3$ (400 mg: 3·0 mmole) to dry ether (20 ml). A soln of the alcohol (**3**) (284 mg: 1·0 mmole) in ether (20 ml) was added with stirring to this mixture. After 20 min, excess hydride was destroyed (EtOAc) and the mixture poured into water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted the sole product (**8**) (250 mg: 90%), identical with that obtained as described under (a).

1-exo-*Hydroxy*-2,2-*dimethyl*[3](1,2)*ferrocenophane* (**10**). Conc H_2SO_4 (2 drops) was added to a stirred soln of the alcohol (**9**) (200 mg: 0·7 mmole) in aqueous acetone (1:1: 20 ml). The mixture was stirred for 15 min, diluted with water (100 ml), and extracted thoroughly with ether. The extracts were washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ether and chromatographed on Al_2O_3. Ligroin–ether (9:1) eluted two well separated yellow bands. The first band afforded starting material (**9**)

(105 mg: 52%). The second band afforded the epimeric alcohol (**10**) (70 mg; 35%), a yellow solid, m.p. 92–93°. (Found: C, 67·1; H, 6·9. $C_{15}H_{18}FeO$ requires: C, 66·7; H, 6·7%). IR 3618 cm^{-1} (OH).

1-*Methoxy-2,2-dimethyl*[3](1,2)*ferrocenophanes* (**11** *and* **12**). The alcohol (**9**) (135 mg: 0·5 mmole) was dissolved in MeOH (10 ml) containing conc H_2SO_4 (3 drops). The soln was stirred for 15 min, diluted with water (50 ml), and extracted thoroughly with ether. The extracts were washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ether and chromatographed on Al_2O_3. Ligroin–ether (24:1) eluted two well separated bands. The first band afforded the *endo*-methoxy compound (**11**) (51 mg: 36%), a yellow solid, m.p. 39–40°. (Found: C, 67·4; H, 6·9. $C_{16}H_{20}FeO$ requires: C, 67·6; H, 7·1%). The second band afforded the *exo*-methoxy compound (**12**) (77 mg: 55%), a yellow liquid. (Found: C, 67·4; H, 6·8. $C_{16}H_{20}FeO$ requires: C, 67·6; H, 7·1%).

1-exo-*Deuterio-2,2-dimethyl*[3](1,2)*ferrocenophane* (**6**). A soln of the alcohol (**9**) (100 mg: 0·35 mmole) in dry ether (20 ml) was added to a stirred suspension of LAD (42 mg: 1·0 mmole) and $AlCl_3$ (270 mg: 2·0 mmole) in dry ether (20 ml). After 20 min, the excess of deuteride was destroyed (EtOAc) and the mixture poured into water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$) and evaporated. The residue was dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted a single yellow band which afforded **6** (79 mg; 89%) as a yellow liquid.

The same compound (identical IR and ^1H NMR) was formed in 90% yield by mixed-deuteride reduction of the *exo*-alcohol (**10**).

1-endo-*Deuterio-2,2-dimethyl*[3](1,2)*ferrocenophane* (**5**). The ketone[9] (**1**) (134 mg; 0·5 mmole) was reduced with LAD in a manner exactly similar to that used for the preparation of alcohol **9** described in a previous experiment. The crude product (IV; R_1 = D, R_2 = OH) (123 mg: 90%) was reduced with mixed-hydride reagent in a manner exactly similar to that described previously for the preparation of **8**. The product was dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted a single yellow band which afforded **5** (80 mg: 90%) as a yellow liquid.

The ^1H NMR spectra of the epimeric compounds (**5** and **6**) were quite distinct (see Table).

2,2-*Dimethyl*[3](1,2)*ferrocenophane* (**4**). The ketone[9] (**1**) (268 mg: 1·0 mmole) in dry ether (20 ml) was added to a stirred suspension of LAH (60 mg; 1·5 mmole) and $AlCl_3$ (400 mg: 3·0 mmole) in dry ether (20 ml). After 20 min, excess hydride was destroyed (EtOAc) and the mixture poured into water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was dissolved in ligroin and chromatographed on Al_2O_3. Ligroin eluted a single yellow band which afforded **4** (245 mg; 95%) as a yellow liquid. (Found: C, 70·8; H, 7·0. $C_{15}H_{18}Fe$ requires: C, 70·9; H, 7·1%).

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