Journal of Organometallic Chemistry, 52 (1973) 407–424

ORGANOMETALLIC COMPOUNDS

XII*. STEREOCHEMICAL INTERCONVERSION REACTIONS BETWEEN 1,1′-BIS(α-HYDROXYALKYL)FERROCENES AND 7-OXA[3]FERROCENOPHANES

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(Received September 19th, 1972)

SUMMARY

Meso and racemic isomers of 1,1′-bis(α-hydroxyalkyl)ferrocene derivatives, and *trans* and *cis* isomers of 7-oxa[3]ferrocenophanes have been isolated. The configurations of these isomers have been determined both by spectroscopy and from their reaction behavior. It has been found that the ring-closure and ring-opening interconversion reactions between 1,1′-bis(α-hydroxyalkyl)ferrocenes and 7-oxa[3]-ferrocenophanes are stereospecific. PMR spectra of the diols and ethers have been examined at 100 MHz in CF_3COOH, and the existence of α-[1′-(α-hydroxyalkyl)-ferrocenyl]carbonium ions has been demonstrated in this acid. A mechanism for the various interconversion reactions is proposed on the basis of their stereospecific reactivity and from the PMR spectra of the carbonium ions.

INTRODUCTION

In a previous paper in this series[1], one of the authors (K.Y.) reported that 1,1′-bis(α-hydroxyethyl)ferrocene could be converted into 1,1′-bis(ethyleneoxy)ferrocene, the so-called 7-oxa[3]ferrocenophane**, on treatment with acid or acidic alumina by means of an intramolecular dehydration cyclization, while (α-hydroxyethyl)ferrocene, the corresponding monosubstituted alcohol, was converted into vinylferrocene under the same conditions. At the same time, similar investigations were also independently reported by several other groups[3]. Formation of the bridged ether by dehydration of 1,1′-bis(hydroxymethyl)ferrocene has also been reported by Rinehart *et al.*[4]

Derivatives of 1,1′-bis(α-hydroxyalkyl)ferrocene with two chiral centers can exist as two stereoisomers with either *meso* and racemic, or *erythro* and *threo* forms. The ethers produced by cyclization of these diols also have two isomers with either a *trans* or *cis* form. However, to date, no report has appeared describing the separation

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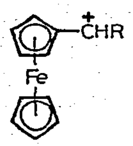
* For Part XI see ref. 8b.

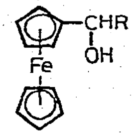
** The system of nomenclature proposed by Smith[2] has been adopted.

of the diols and ethers into stereoisomers except for a paper by Pauson *et al.*[5], who separated the diphenyl and dimethyl ether derivatives into two compounds but did not determine their configuration.

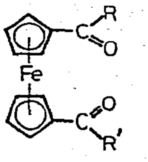
On the other hand, it is known[6] that unusually stable α-ferrocenylcarbonium ions (I) are formed as intermediates in the solvolysis reaction of (α-hydroxyalkyl)-ferrocene derivatives (II). The structure of the ions and the origin of their stability have been discussed on the bases of their PMR spectra[7,8] and reactivity[9]. However, no one has studied the reaction of 1,1′-bis(α-hydroxyalkyl)ferrocene derivatives in relation to the ferrocenylcarbonium ion.



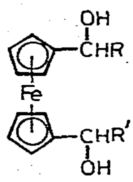
(I) (a) R = H
(b) R = Me
(c) R = Ph
(d) R = i-Pr



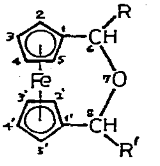
(II) (a) R = H
(b) R = Me
(c) R = Ph
(d) R = i-Pr



(III) (a) R = R′ = OH
(b) R = R′ = Me
(c) R = R′ = Ph
(d) R = Me, R′ = Ph
(e) R = R′ = i-Pr



(IV) R = R′ = H
(V) R = R′ = Me
(VI) R = R′ = Ph
(VII) R = Ph, R′ = Me
(VIII) R = R′ = i-Pr



(IX) R = R′ = H
(X) R = R′ = Me
(XI) R = R′ = Ph
(XII) R = Ph, R′ = Me
(XIII) R = R′ = i-Pr

In the present work, 1,1′-bis(α-hydroxyalkyl)ferrocene derivatives (IV)–(VIII) have been prepared by the reduction of 1,1′-diacylferrocene (IIIa–e), and some of the diols separated into the two isomers as pure crystals by recrystallization. 7-Oxa[3]ferrocenophanes (IX)–(XIII) have been obtained by treatment of the corresponding diols with dilute acid, and four of the ethers [(X)–(XIII)] separated into the two *trans* and *cis* isomers by column chromatography. Their configurations have been determined by means of PMR spectrometry. It has also been found that the C–O–C bond in some ethers is opened by treatment with acidic alumina to give the corresponding diols. The reaction mechanism is discussed below on the basis that these ring-closure and ring-opening reactions proceed stereospecifically*. Furthermore, the PMR spectra of the diols and ethers in 100% trifluoroacetic acid have confirmed that stable α-ferrocenylcarbonium ions are formed in strong acid media, and that the

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* Preliminary results have been reported[10].

structure of the stable species corresponds to that of the intermediates formed in the ring-closure and ring-opening reactions, both by an application of the results of (monohydroxyalkyl)ferrocene derivatives (IIa–c) reported previously[8a] and by means of decoupling.

RESULTS AND DISCUSSION

The intramolecular dehydration reaction of 1,1′-*bis*(α-*hydroxyalkyl*)*ferrocene and its stereochemistry*

Reduction of 1,1′-diacetylferrocene (IIIb) with $LiAlH_4$ gave 1,1′-bis(α-hydroxyethyl)ferrocene (V), m.p. 69–70°, as described earlier[1,11,12]. In the PMR spectrum of the diol, the methyl and methine signals appeared as a quartet of equal intensity and an octet with an intensity ratio of 1/1/3/3/3/3/1/1, respectively. This spectrum suggests that the diol is a mixture of *meso* and racemic isomers. Recrystallization of the diol 7–8 times from hexane gave (Va) as orange-yellow needles, m.p. 99.5–100.5°. The mother liquor from the above recrystallization was chromatographed on alumina, and the initial part of the broad diol band was recrystallized from hexane to give a diol (Vb), m.p. 86–86.5°. These two compounds were confirmed as the *meso* and racemic stereoisomers from elemental analysis and from PMR and IR spectroscopy.

On treatment of the diol (V) with dilute HCl in benzene, the corresponding ether was easily formed[1,3] by intramolecular dehydration. The product was chromatographed giving two bands. The ethers from the first and second bands had m.p. 108.5–109° (Xa) and 107.5–108° (Xb), respectively. PMR and IR spectra indicated that these two ethers were the *trans* and *cis* stereoisomers. Pauson *et al.*[5] also effected the separation of the same isomers, but did not establish their configurations[5,*].

According to the literature[13], 1,1′-bis(α-hydroxybenzyl)ferrocene (VI) has a m.p. 135–136°. In fact, the crude product from the reduction of 1,1′-dibenzoylferrocene (IIIc) melted at ca 135° after recrystallization. The PMR spectrum of the diol, however, exhibits the methine protons as two singlets with the relative intensity ratio of 1/9 at δ 5.51 and 5.44 ppm. This suggests, therefore, that the diol should consist of two isomers in the same ratio. Repeated recrystallization of the diol, m.p. 135–136°, gave yellow needles (VIb), m.p. 121–122°, as pure crystals. The methine protons of the diol (VIb) resonated as a singlet at δ 5.44 ppm indicating that the singlet at δ 5.51 ppm was the methine proton signal of the second isomer (designated as (VIa)). Attempts to separate the other isomer from the mother liquor by recrystallization and chromatography gave only an equivalent mixture of two isomers, m.p. 127–128°, in which the signals of the methine protons were of equal intensity.

The ring-closure reaction of the diol (VI) afforded two ethers which could be separated by chromatography into two bands. The first band afforded ether (XIa), m.p. 197–197.5°, while the second band provided (XIb), m.p. 194.5–195.5°**.

Reduction of 1-acetyl-1′-benzoylferrocene (IIId), prepared by the benzoylation of acetylferrocene, gave an equivalent mixture of *erythro*- and *threo*-diols in which the methyl protons and the methine adjacent to the phenyl group appeared as two

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[*] According to a private communication from Prof. Pauson, their ethers, m.p. 105–107° and m.p. 103–105°, were identical to compounds (Xa) and (Xb) described in the present paper as far as their IR spectra were concerned.

[**] The ethers reported by Pauson *et al.* were of m.p. 195–197° and 184–186°, respectively.

doublets and two singlets, respectively. The diols were recrystallized from a solvent which had been freed from any acid contaminant to give two diols, m.p. 135–136.5° (VIIa) and 136–137.5° (VIIb) respectively. The ether obtained from diol (VII) was also separated into two isomers; the first with a m.p. 158–159° (XIIa) and the other of m.p. 135–136° (XIIb).

Diol (VIII) obtained by the reduction of 1,1′-diisobutyrylferrocene (IIIe) was also expected to exist as two stereoisomers. In spite of repeated recrystallization of the compound, however, the melting point and PMR and IR spectra remained unchanged. The two diisopropyl ethers (XIII) obtained by the dehydration of (VIII) with dilute HCl had m.p. 89–90° (XIIIa) and 66–67° (XIIIb) respectively. The PMR spectra of the ethers contained signals corresponding to the methyl protons which appeared as two doublets [(XIIIa): δ 0.81 and 1.15 ppm; (XIIIb): δ 0.90 and 1.12 ppm] which

TABLE 1

DATA RELATING TO THE PMR SPECTRA OF 1,1′-BIS(α-HYDROXYALKYL)FERROCENES AT 100 MHz IN $CDCl_3$ (δ, ppm)

Substituents	*Compounds*				*OH*	*OH*
		$C\underline{H}_3-$	$-C\underline{H}_2-$	$(CH_3)_2C\underline{H}-$	$-C\underline{H}-$	$PhC\underline{H}-$
H	(IV)		4.39(s)			
Me	(Va) (*meso*)	1.40(d)			4.65(q)	
Me	(Vb) (racemic)	1.42(d)			4.62(q)	
Ph	(VIa) (*meso*)					5.51(s)
Ph	(VIb) (racemic)					5.44(s)
Ph+Me	(VIIa) (*erythro*)	1.27(d)			4.65(q)	553(s)
Ph+Me	(VIIb) (*threo*)	1.40(d)			4.59(q)	5.49(s)
i-Pr	(VIII)	0.81(d) 0.89(d)		1.72(m)	4.15[a]	

[a] The signal overlaps with the ring proton signals.

TABLE 2

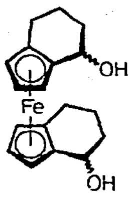
DATA RELATING TO THE PMR SPECTRA OF 7-OXA[3]FERROCENOPHANES AT 100 MHz IN $CDCl_3$ (δ, ppm)

Substituents	*Compounds*				*O*	*O*
		$C\underline{H}_3-$	$-C\underline{H}_2-$	$(CH_3)_2C\underline{H}-$	$-C\underline{H}-$	$PhC\underline{H}-$
H	(IX)		3.90(s)			
Me	(Xa) (*trans*)	1.50(d)			3.80(q)	
Me	(Xb) (*cis*)	1.45(d)			4.32(q)	
Ph	(XIa) (*trans*)					5.03(s)
Ph	(XIb) (*cis*)					5.46(s)
Ph+Me	(XIIa) (*trans*)	1.62(d)			4.01(q)	4.74(s)
Ph+Me	(XIIb) (*cis*)	1.56(d)			4.71(q)	5.07(s)
i-Pr	(XIIIa) (*trans*)	0.81(d) 1.15(d)		1.87(m)	3.15(d)	
i-Pr	(XIIIb) (*cis*)	0.90(d) 1.12(d)		2.00(m)	3.61(d)	

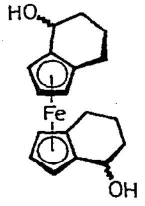
were attributed to the two methyls in the isopropyl group being diastereomeric to each other due to the presence of a chiral carbon in the α-position[14]. On the other hand, the PMR spectrum of diol (VIII) contained only two doublets corresponding to the methyl protons (δ 0.81 and 0.89 ppm) in spite of, presumably, the presence of a mixture of two isomers, while the methyl protons of (α-hydroxyisobutyl)ferrocene (IId), the corresponding mono-ol, appeared as two doublets (δ 0.75 and 0.87 ppm in CCl_4).

Egger and Falk[15] have reported that 1,1,1',1'-bis(α-oxotetramethylene)-ferrocene consists of two stereoisomers of *meso* and racemic form, each of which was reduced with $LiAlH_4$ to give two isomers corresponding to the *endo,endo* and *endo,exo* diols due to the configuration of the OH groups. The *endo,endo* diol (XIV) (from the *meso*-ketone) and (XV) (from the racemic ketone) could not be ether-linked by treatment with dilute HCl, but were converted into cyclic vinyl compounds [(XVI) and (XVII), respectively] through dehydration involving the homo-annular rings[16]. This is presumably due to steric hindrance or to the ready formation of the α-ferrocenyldicarbonium ion[17,*].

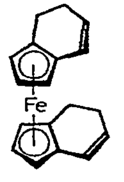
The ethers (X)–(XIII) with chiral substituents could also be separated into two isomers. In the PMR spectra of these isomers, the methine proton signals appeared in higher fields (0.3–0.7 ppm) in the ethers (Xa), (XIa), (XIIa) and (XIIIa) which were eluted as the first band during chromatographic separation than in the ethers (Xb), (XIb), (XIIb) and (XIIIb) which were eluted as the second band. From a consideration of steric hindrance and C–O–C bond strain using stereomodels[**], the most preferred conformations in the *trans* and *cis* forms of the ethers were expected to be those depicted in (XVIII) and (XIX), respectively. For this reason, the paramagnetic anisotropy of the cyclopentadienyl (Cp) ring would be more effective for the methine proton of the *cis*-ether than for that of the *trans*, since the latter lies above the Cp ring plane. This confirms the assignment of the ethers (Xa)–(XIIIa) and (Xb)–(XIIIb) to *cis* and *trans* forms respectively. Further, from conformation (XVIII) and (XIX), it is not un-



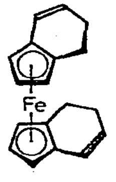
(XIV)



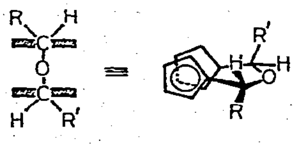
(XV)



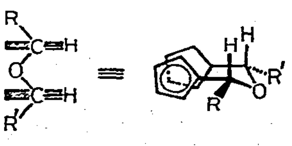
(XVI)



(XVII)



(XVIII)



(XIX)

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[*] The PMR spectrum of 1,1'-bis(α-hydroxyisopropyl)ferrocene in strong acid suggested the formation of a di-cation.

[**] H.G.S. and Dreiding ferrocene stereomodels supplied by Maruzen Co., Tokyo, Japan and by Büchi Glasapparatefabrik, Switzerland, respectively, were used.

reasonable to expect that the methyl proton signals of the *trans*-ethers (Xa) and (XIIa) would appear at slightly lower fields (ca. 0.05 ppm) than those of the *cis*-ethers (Xb) and (XIIb) in the PMR spectrum, contrary to the behaviour of the methine protons.

In the PMR spectra of the diols, the methine protons of (Va), (VIa) and (VIIa) appear at lower fields than those of (Vb), (VIb) and (VIIb). The former diols have the same configuration while the latter diols belong to another configurational group. It is difficult, however, to determine the configuration of the diols from their chemical shifts alone. The IR spectra of the diols in dilute CCl_4 solution exhibit differences in the ratio of the optical density corresponding to the absorption of free and intramolecularly hydrogen-bonded OH groups (D_B/D_F) for the two isomers present; 0.670 and 0.603 (0.50×10^{-3} mol/l) for (Va) and (Vb), and 0.921 and 0.778 (0.50×10^{-3} mol/l) for (VIIa) and (VIIb), respectively[18]. These observations may be explained on the basis of the difference in preferred conformation caused by different configurations at the two chiral carbon atoms[19,*]. From the IR data, using a stereomodel, it may be deduced that the configurations of the diols (Va) and (Vb) correspond to the *meso* and racemic forms, respectively, and that those of the diols (VIIa) and (VIIb) correspond to the *erythro* and *threo* forms[19,20,**]. By analogy with the above two diols, diol (VIb) whose methine proton signal appears at a higher field in the PMR spectrum than that of the other diol, should be the racemic form, and diol (VIa), which could not be isolated, is the *meso* form. This assignment is also supported by the stereochemistry of the interconversion reaction, as described below.

The intramolecular ring-closure reaction of diols (V)–(VII) induced by treatment with dilute HCl proceeds stereochemically to the corresponding ethers (X)–(XII). The yields of ethers obtained from the *meso*-diol (Va) were 29% for *trans*-(Xa) and only 3.3% for *cis*-(Xb), while those from the racemic diol (Vb) were 1.5% and 26% for *trans*-(Xa) and *cis*-(Xb), respectively. In the case of diol (VII), the *trans*/*cis* ratio for ethers (XII) produced from the *erythro*-diol (VIIa) and the *threo*-diol (VIIb) were 6.7 and 0.1, respectively. The ring-closure reaction of diol (VII) proceeded much more readily than that of the other diols, diol (VII) being, in fact, converted to the ether during the measurement of its PMR spectrum in commerical $CDCl_3$. Conversion of diol (VIb) to the corresponding ether led to the formation of the *trans*-ether in 4.5% yield and the *cis*-ether in 41% yield.

Ring-opening reactions of 7-oxa[3]ferrocenophane derivatives

The ether linkage in the 7-oxa[3]ferrocenophanes (X) and (XI) produced from the corresponding diols was capable of being opened by treatment with acidic alumina in benzene over a period of time to yield compounds (V) and (VI). When a solution of the *trans*-ether (Xa) in benzene was stirred with acidic alumina contaminated with a small amount of H_2O for 5 days, diol (V), which according to its IR spectrum consisted almost entirely of the *meso*-diol (Va), was obtained in 24% yield together with the unchanged *trans*-ether (53%) and a small amount of the *cis*-ether. On the other hand, similar treatment of the *cis*-ether (Xb) gave diol (V) (37%), which consisted chiefly of the racemic diol (Vb), the *trans*-ether (5.6%) and unchanged *cis*-ether (34%).

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[*] The values of D_B/D_F in 2,4-pentanediol are 1.18 and 0.70 for the *meso* and racemic forms, respectively.

[**] In 1,3-diols and 3-amino alcohols, the values of D_B/D_F are, in general, lower for the *threo* form than for the *erythro* form.

Ring-opening of ether (XI) was more difficult to accomplish than that of ether (X), and was not reproducible. On treatment of *trans*-ether (XIa) under the same conditions the yield of diol (VI) was only 5% and most of the starting material was recovered unchanged (83%). Similar reaction of *cis*-ether (XIb) gave diol (VI) (13%), which consisted of the *meso* and racemic isomers in 1/5 ratio, and also *trans*-ether (2.2%), in addition to unchanged starting material (79%).

Treatment of ether (XII), whose substituents were a methyl and a phenyl group, with an acidic catalyst failed to give the corresponding diol even on varying the reaction conditions, only the initial ether being recovered.

The mechanism of the interconversion process and PMR spectrometric studies[21]

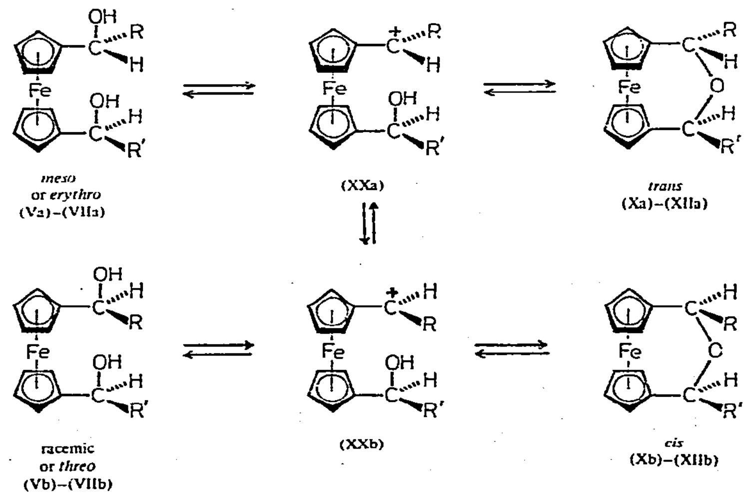
The experimental results described above may be summarised as follows. Both ring-closure and ring-opening reactions involving diols and ethers proceed in an almost stereochemical fashion; *meso*- or *erythro*-diol ⇄ *trans*-ether, and racemic or *threo*-diol ⇄ *cis*-ether. In addition, in the ring-opening reaction, an isomeric ether different from the initial ether was obtained but only in low yield whilst the diol obtained was a mixture of *meso* and racemic isomers.

Richards and Hill[6] have confirmed that the solvolysis of (α-hydroxyalkyl)-ferrocene derivatives proceeds via a first-order reaction mechanism. On the basis that the present reactions also conform to an S_N1 reaction, it is possible to present a mechanism as shown in Scheme 1.

The equilibrium (XXa) ⇄ (XXb) is supported by the fact that the products of the ring-closure reaction contained the isomeric form of the starting compound. Although diol (VII) was not obtained from ether (XII), from the PMR spectrum it was indicated that in strong acid the ether ring was opened, as described below. It is possible that the substituent effect in the intermediate may displace the equilibrium formed during the interconversion reaction towards the formation of ether (XII).

SCHEME 1

MECHANISM OF THE INTERCONVERSION REACTION BETWEEN 1,1'-BIS(α-HYDROXYALKYL)FERROCENES AND 7-OXA[3]FERROCENOPHANES IN THE PRESENCE OF AN ACIDIC CATALYST



In order to confirm the formation of intermediates (XXa) and (XXb), as described above, the PMR spectra of the diols and ethers dissolved in trifluoroacetic acid (TFA) were studied. Unless otherwise stated, all PMR spectra described below are those of the diols and ethers in TFA. The spectra obtained are shown in Figs. 1–4.

The spectra of diol (IV) and ether (IX) are identical (see Fig. 1a). Thus it follows that the same species is formed in TFA solutions of both diol (IV) and ether (IX). The six signals in the spectrum have the same relative intensity, the A, C, D and F signals which are split into triplets being those of the ring protons, while the two sharp singlets B and E are assigned to the two methylene groups. Irradiation of signal A changed signal F into a sharp singlet, but the other signals were unchanged (Fig. 1b). Irradiation of signal C changed only signal D into a sharp singlet (Fig. 1c). Consequently, signals A and F arise from four protons in the same ring (designated ring A), and signals C and D are assigned to the protons of the other ring (designated ring B). The chemical shifts of signals A, E and F are similar to those of the corresponding α-ferrocenylcarbonium ion (Ia) (δ 4.72, triplet; 5.95, singlet; and 6.32, triplet; in ppm)^{8a}. It may thus be deduced that the carbon atom in the α-position in the sub-

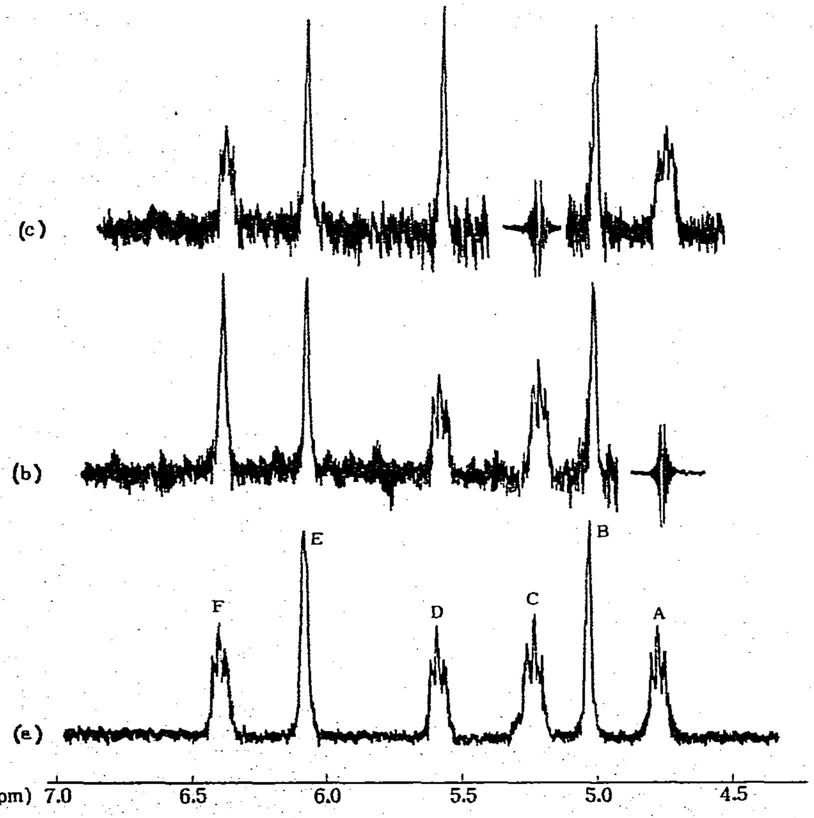


Fig. 1. PMR spectra, recorded at a sweep width of 9 × 1/5 ppm, of 1,1'-bis(hydroxymethyl)ferrocene(IV) or 7-oxa[3]ferrocenophane(IX) in trifluoroacetic acid; (a) original spectrum; (b) and (c) spectra irradiated at signals A and C, respectively.

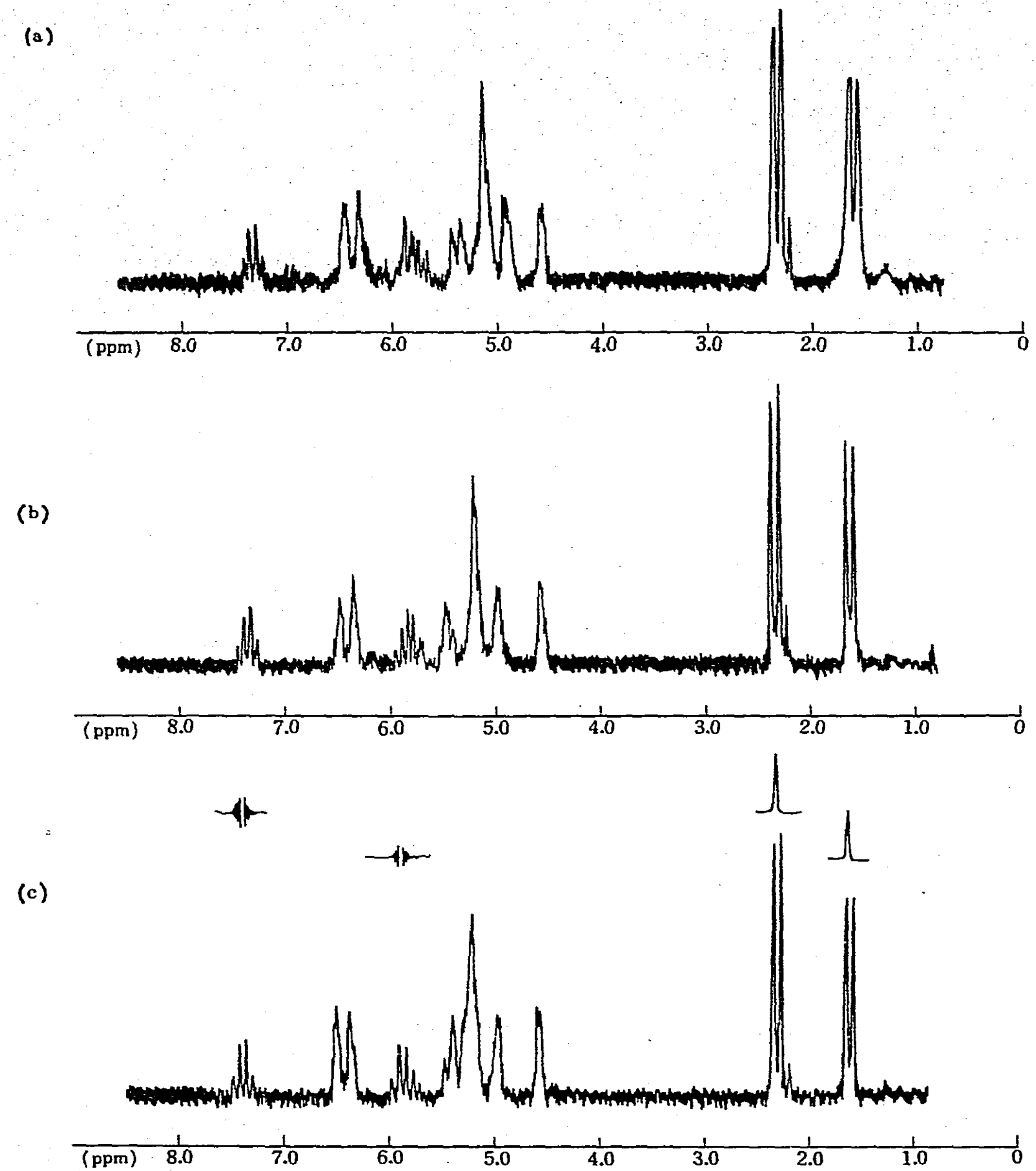


Fig. 2. PMR spectra of 1,1'-bis(α-hydroxyethyl)ferrocene (V) or 6,8-dimethyl-7-oxa[3]ferrocenophane (X) in trifluoroacetic acid; (a) mixture of *meso* and racemic diols(V) in a 1/1 ratio; (b) *meso*-diol (Va) or *trans*-ether (Xa); (c) racemic diol (Vb) or *cis*-ether (Xb).

stituent in the A-ring is a cationic centre, and that the other ring moiety does not have a completely cationic centre because of the higher chemical shifts of the ring and methylene protons than those corresponding to the α-carbonium ion (Ia). For this reason, it follows that the species present in TFA solution has the monocationic structure depicted in (XX) (R=R'=H).

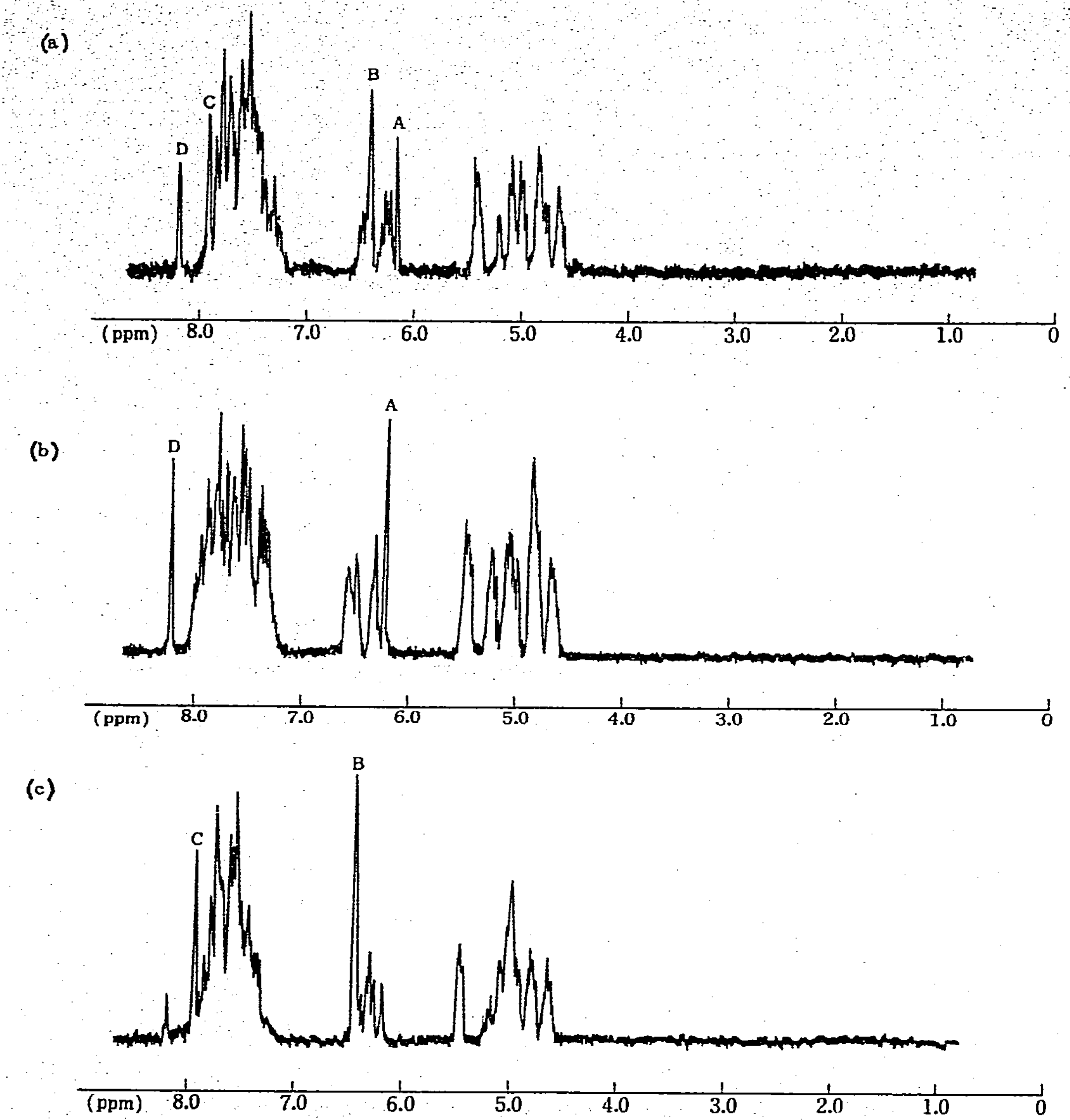


Fig. 3. PMR spectra of 1,1′-bis(α-hydroxybenzyl)ferrocene (VI) or 6,8-diphenyl-7-oxa[3]ferrocenophane(XI) in trifluoroacetic acid; (a) mixture of *meso* and racemic diols(VI) in a 1/1 ratio; (b) *trans*-ether (XIa); (c) racemic diol (VIb) or *cis*-ether (XIb).

The spectra of *trans*-ether (XIa) and *cis*-ether (XIb) exhibit different patterns when measured immediately after sampling.

In both ethers, two methine signals are observed; δ 6.13 (A) and 8.12 ppm (D) in *trans*-(XIa), and δ 6.38 (B) and 7.87 ppm (C) in *cis*-(XIb) (Fig. 3b and c). In the *trans*-ether, peaks B and C appeared and developed with time, while peaks A and D did so in the *cis*-ether. After 60 min, the spectra of both the *trans* and *cis* isomers became

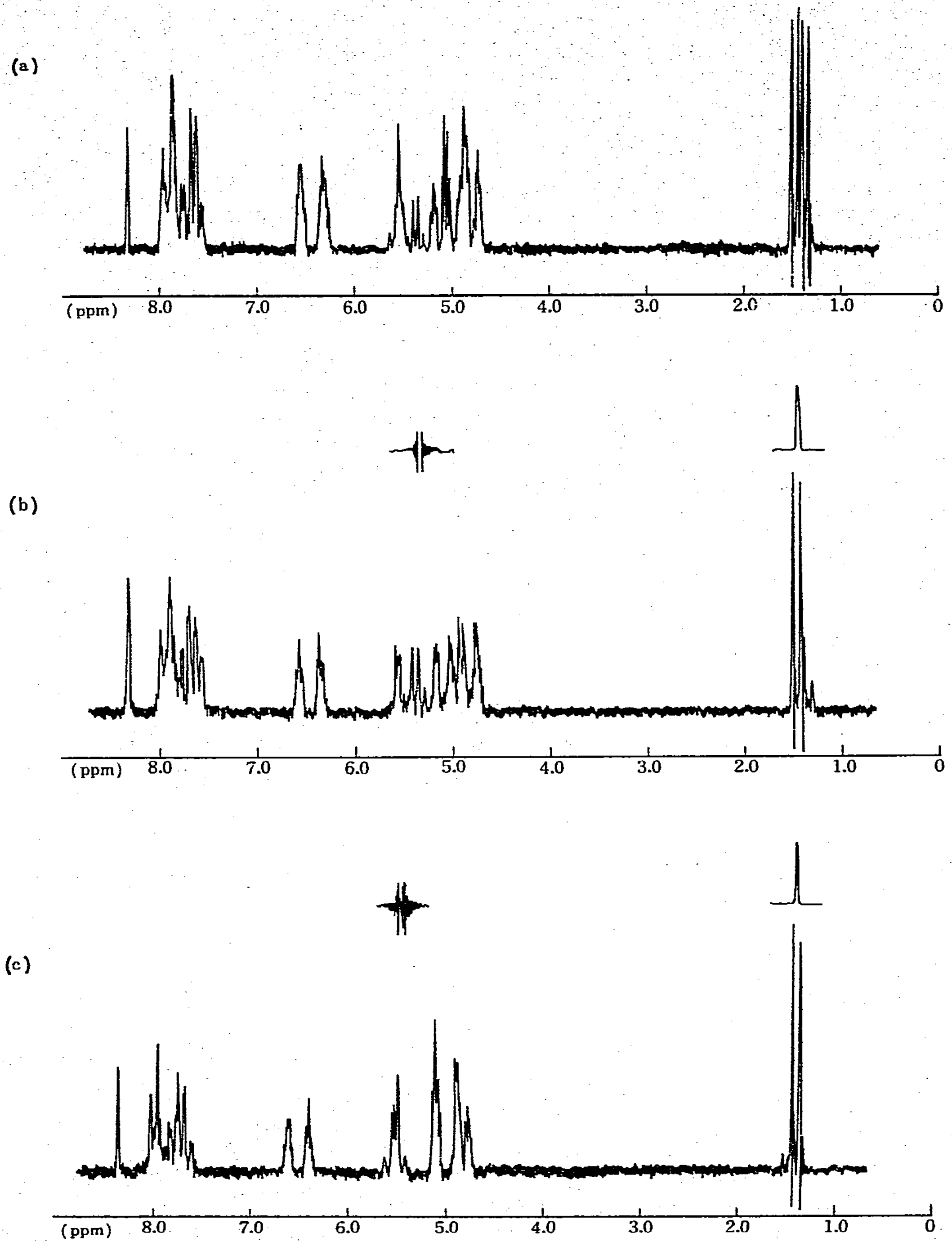
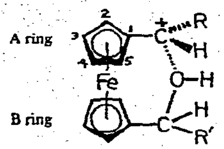
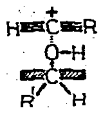


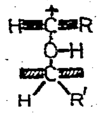
Fig. 4. PMR spectra of 1-(α-hydroxybenzyl)-1'-(α-hydroxyethyl)ferrocene (VII) and 6-phenyl-8-methyl-7-oxa[3]ferrocenophane (XII) in trifluoroacetic acid; (a) mixture of *erythro* and *threo*-diols (VII) in a 1/1 ratio; (b) *erythro*-diol (VIIa) or *trans*-ether (XIIa); (c) *threo*-diol (VIIb) or *cis*-ether (XIIb).



(XX)



(XXa)



(XXb)

superimposed being identical with the spectrum obtained for the mixture of *meso* and racemic diol (VI) (Fig. 3a). In addition, the spectrum of the racemic diol (VIb) was identical with that of *cis*-ether (XIb) (Fig. 3c). On the basis of the spectra of model compounds (IV) and (IX) and that of the α-ferrocenylcarbonium ion (Ic) (methine proton: δ 8.09 ppm), the two methine signals C and D are assigned to the methine protons attached to the cationic carbon atom (A-ring moiety). The fact that the spectra of the *trans* and *cis* isomers are different from each other but agree with those of the *meso*- and racemic diols respectively suggests that the ether and diol species present in solution are the same and have configurations reflecting those of the original ethers and diols. The species from the *trans*- and *cis*-ether isomerize in time by rotation about the C–C bond between the Cp ring and the bond involving the cationic carbon atom. Hence, the stereochemical configurations of these species in solution are as depicted in (XXa) and (XXb). The methine proton in the B-ring moiety of the *trans* species (XXa) should be shielded by the phenyl ring in the A-ring moiety, and hence resonate at a higher field than the proton of the *cis* isomer (XXb). The methine proton in the A-ring moiety of the *trans* species may be deshielded by the phenyl group in the B-ring moiety since the methine proton would be in the paramagnetic anisotropic zone of the phenyl group (Table 3).

The spectra of the *trans*-ether (Xa) and *cis*-ether (Xb) with two substituted methyl groups were different from each other with respect to the Cp ring proton absorptions in the region near δ 5.4 and 5.8 ppm (Fig. 2). Both methyl and methine proton absorptions appeared in the two regions, and by means of decoupling, it was con-

TABLE 3

DATA RELATING TO THE PMR SPECTRA OF α-[1'-(α-HYDROXYALKYL)FERROCENYL]CARBONIUM IONS IN TRIFLUOROACETIC ACID AT 100 MHz (δ, ppm)

Substituents	*Isomer*	*A-ring moiety*						*B-ring moiety*			
		Cp ring protons				$\geq CH$	$-CH_3$	*CP ring protons*[a]		$\geq CH$	$-CH_3$
		H_5	H_2	H_4	H_3						
H		4.78	4.78	6.41	6.41	6.09		5.24(2)	5.60(2)	5.04	
Me	*trans*	4.56	4.95	6.30	6.43	7.32	2.31	5.15(3)	5.41(1)	5.78	1.62
Me	*cis*	4.55	4.94	6.29	6.44	7.32	2.31	5.16(3)	5.35(1)	5.82	1.62
Ph	*trans*	4.81	5.41	6.21	6.45	8.12		4.63(1) 5.04(1)	4.75(1) 5.16(1)	6.13	
Ph	*cis*	4.81	5.41	6.26	6.38	7.87		4.63(1) 5.06(1)	4.95(2)	6.38	
Ph+Me	*trans*	4.87	5.56	6.31	6.51	8.29		4.74(1) 5.01(1)	4.91(1) 5.17(1)	5.36	1.49
Ph+Me	*cis*	4.87	5.58	6.31	6.51	8.31		4.74(1) 5.07(2)	4.87(1)	5.59	1.40

[a] Numbers in parentheses indicate relative intensity of signals.

firmed that the methyl protons in the lower field (δ 2.31 ppm) interact with the methine proton in the lower field (δ 7.32 ppm), and that both groups are bonded to the cationic carbon atom in models (XXa) and (XXb). The set of methyl and methine groups in the higher field of the spectrum (δ 1.62 and 5.78 or 5.82 ppm) should correspond to those in the B-ring moiety. The spectra of the *meso*-diol (Va) and the racemic (Vb) were found to be the same as those of the *trans*- and *cis*-ethers, respectively. Both spectra (Fig. 2b and c) changed with time and ultimately corresponded to the spectrum of the mixed diol of *meso* and racemic forms. It is considered that the small difference between the spectra of the two isomers is due to the smaller magnetic effect of the methyl group relative to the phenyl.

With compounds containing a substituted phenyl and methyl group, the spectra of the *trans*- and *cis*-ethers were identical to those of the *erythro*- and *threo*-diols, respectively (Fig. 4b and c), both spectra being time dependent and ultimately transforming to the spectra of the mixture of diol or ether (Fig. 4a) after about 80 min. Contrary to expectation, the signals of the methyl and methine protons in the *erythro*- and *threo*-diols appeared in only one field region, in contrast to the behaviour observed with other compounds. The methine proton adjacent to the phenyl group exhibited a chemical shift (*erythro*, δ 8.29; *threo*, δ 8.31 ppm) close to that of the phenyl derivative of the α-carbonium ion (Ic) (δ 8.09 ppm), whereas the signals of the methyl group (δ 1.49 and 1.40 ppm) and the methine (δ 5.36 and 5.59 ppm)* adjacent to the methyl group appeared at a considerably higher field than that of the methyl derivative of the α-carbonium ion (Ib) (methyl, δ 2.25; methine, δ 7.12 ppm). From this it was concluded that an α-carbon attached to a phenyl group is converted exclusively to a cationic center, whereas an α-carbon attached to a methyl group is not. This behavior may be attributed to the different electronic effects generated by the two substituents.

The chemical shifts of the ring protons in each compound were determined by comparison of the isomers and by analogy with the corresponding α-ferrocenylcarbonium ion (I). The results are summarized in the Table 3.

It has in fact been queried as to whether a species in 100% TFA, which is a strong acid, may be considered as a real intermediate formed in the reaction[7b]. However, its inclusion in the mechanism suggested for this reaction is supported by the fact that the spectra of the ethers and diols in TFA agree stereochemically with each other, and that each isomeric species formed in the system undergoes isomerization with time. For this reason, it is not unreasonable to assume that the intermediates formed in the interconversion reaction of the diols and ethers (Scheme 1) exist as real chemical species in TFA solution.

The PMR spectra of the cyclic diols (XIV) and (XV) in TFA have also been examined, but these spectra were complex and changed rapidly with time. It is suggested that these diols are rapidly converted to the corresponding vinyl compounds (XVI) and (XVII) through dehydration involving two water molecules, or alternatively that the species formed in TFA are unstable and decompose readily.

EXPERIMENTAL

All m.p.'s are uncorrected. Chromatographic separation was carried out using Wako activated alumina (300 mesh) unless otherwise stated.

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* This signal overlapped with the ring proton signal. Its chemical shift was determined by decoupling.

IR spectra were measured using a Hitachi Perkin–Elmer model 225 grating infrared spectrophotometer employing the KBr disk method. All PMR spectra were measured on a JEOL-JNM-4H-100 spectrometer at 100 MHz at room temperature with TMS as an internal reference. Normal spectra were run using a field/frequency stabilized mode. For double-resonance experiments, a JEOL-JNM-SD-30 spin decoupler instrument was used and the spectra were recorded at a sweep width of 9×1 or $9 \times \frac{1}{5}$ ppm over a period of 5 min using frequency sweep. Chemical shifts were calibrated using a digital frequency counter. PMR data of all original compounds were measured in $CDCl_3$ as a solvent. The spectra of α-ferrocenylcarbonium ions were recorded immediately after dissolution of the corresponding diols or ethers in commercial 100% trifluoroacetic acid at temperatures below −10° (concentration about 5% w/v).

The isomer ratios, *meso*/racemic, of the diols were determined from the relative intensity of the methyl or methine proton signals in the PMR spectra, or from the out-of-plane absorptions of the CH band in the Cp ring in the IR spectra.

Preparation of ketones

The ketones and acids, which were used as starting materials for the synthesis of the corresponding diols, were prepared according to reported or modified procedures. Each sample of 1,1'-ferrocenedicarboxylic acid (IIIa), m.p. 250° (dec.) [lit.[1] m.p. 240° (dec.)], 1,1'-diacetylferrocene (IIIb), m.p. 126–127.5° (lit.[22] m.p. 127.5–128.5°), 1,1'-dibenzoylferrocene (IIIc), m.p. 106–107° (lit.[13] m.p. 106.5–106.7°), 1-acetyl-1'-benzoylferrocene (IIId), m.p. 69–69.5° (lit.[23] m.p. 71–72°), and 1 1'-diisobutylferrocene (IIIe), m.p. 49–51° (lit.[24] m.p. 50–51°) was identified by IR and PMR spectrometry. Bis(α-oxotetramethylene)ferrocene was prepared by dehydration of 1,1'-bis(α-carboxypropyl)ferrocene with trifluoroacetic anhydride. The diketone was chromatographed on alumina and thus separated into the *meso* and racemic forms, m.p. 170–170.5° and 156–157°, respectively (lit.[15] *meso*: m.p. 170°, racemic: m.p. 160°].

Preparation of diols

Each diol was prepared by reduction of the corresponding ketone or acid with $LiAlH_4$ according to the routine method[1].

1,1'-*Bis(hydroxymethyl)ferrocene* (*IV*). The diol (IV) was obtained almost quantitatively from 1,1'-ferrocenedicarboxylic acid (IIIa). It had m.p. 107–108° [lit.[4] m.p. 107–108°].

1,1'-*Bis(α-hydroxyethyl)ferrocene* (*V*). The crude diol (m.p. 69–71°) was prepared by reduction of 1,1'-diacetylferrocene (IIIb) with $LiAlH_4$, and was additionally recrystallized eight times from hexane as orange-yellow needles, m.p. 99.5–100.5° [(Va); *meso*-diol]. (Found: C, 61.47; H, 6.40. $C_{14}H_{18}FeO_2$ calcd.: C, 61.34; H, 6.62%.) IR spectrum (cm^{-1}): 3300 [ν(OH)], 1363 [$\delta(CH_3)$], and 803 [δ(CH) of Cp].

The mother liquor from the above recrystallization was evaporated, the residue chromatographed using AcOEt as the eluant, and the initial part of the broad band of the diol recrystallized four times from hexane as orange-yellow needles, m.p. 86–86.5° [(Vb); racemic diol]. (Found: C, 61.07; H, 6.45. $C_{14}H_{18}FeO_2$ calcd.: C, 61.34; H, 6.62%.) IR spectrum (cm^{-1}): 3230 [ν(OH)], 1366 [$\delta(CH_3)$] and 814 [δ(CH) of Cp].

The diol recorded in the literature (m.p. 69–71°)[1,11] is obviously a mixture of *meso* and racemic isomers in 1/1 ratio.

1,1'-Bis(α-hydroxybenzyl)ferrocene (VI). Repeated recrystallization of the diol obtained by the reduction of 1,1'-dibenzoylferrocene (IIIc) gave orange-yellow needles, m.p. 121–122° [(VIb); racemic diol]. (Found: C, 72.11; H, 5.28. $C_{24}H_{22}FeO_2$ calcd.: C, 72.38; H, 5.57%.) IR spectrum (cm^{-1}): 3270 [ν(OH)], 1599 [ν(C=C) of Ph] and 806 [δ(CH) of Cp].

The mother liquor from the above recrystallization was chromatographed on alumina using AcOEt as the eluant. On recrystallization of the latter part of the alcohol band, two kinds of crystals, the first consisting of orange-yellow prisms, m.p. 128–128.5° and the second consisting of yellow needles, m.p. 125–130°, were obtained. The former was a mixture of the *meso*- and racemic diols in a 1/1 ratio, while the latter was almost completely the racemic diol. An attempted isolation of the *meso*-diol was unsuccessful despite repeated recrystallization or chromatography.

The crude diol (VI), m.p. 134–136°, which possessed a similar melting point to that described in the literature[13], proved to be mixture of the *meso* and racemic diols in 1/9 ratio.

1-(α-Hydroxybenzyl)-1'-(α-hydroxyethyl)ferrocene (VII) The $LiAlH_4$ reduction product of 1-acetyl-1'-benzoylferrocene (IIId) was recrystallized five times from a hexane/benzene mixture to yield orange-yellow needles, m.p. 136–137.5° [(VIIb); *threo*]. (Found: C, 68.41; H, 5.98. $C_{19}H_{20}FeO_2$ calcd.: C, 67.88; H, 6.00%.) IR spectrum (cm^{-1}): 3250 [ν(OH)], 1599 [ν(C=C) of Ph], 1366 [$\delta(CH_3)$], and 805 [δ(CH) of Cp].

The mother liquor from the first recrystallization was recrystallized three times from a hexane/benzene mixture to yield orange-yellow needles, m.p. 135–136.5° [(VIIa); *erythro*]. (Found: C, 68.64; H, 5.87; M^+ 336.0796. $C_{19}H_{20}FeO_2$ calcd. C, 67.88; H, 6.00%; M 336.0803.) IR spectrum (cm^{-1}): 3280 [ν(OH)], 1600 [ν(C=C) of Ph], 1371 [$\delta(CH_3)$], and 811 [δ(CH) of Cp].

The crude reduction product was a mixture of the *erythro*- and *threo*-diols in 1/1 ratio.

1,1'-Bis(α-hydroxyisobutyl)ferrocene (VIII). The diol was synthesized by reduction of 1,1'-diisobutyrylferrocene (IIIe), and recrystallized from a hexane/benzene mixture as orange-yellow prisms (VIII), m.p. 124–125°. (Found: C, 65.80; H, 7.95. $C_{18}H_{26}FeO_2$ calcd. C, 65.46; H, 7.94%.) IR spectrum (cm^{-1}): 3240 [ν(OH)], 1382 and 1364 [$\delta(CH_3)$ of i-Pr], and 815 [δ(CH) of Cp].

1,2,1',2'-Bis(α-hydroxytetramethylene)ferrocene, (XIV) and (XV). Reduction of *meso*- and racemic bis(α-oxotetramethylene)ferrocene gave mostly the *endo,endo* isomer of (XIV), m.p. 140–143.5° (lit.[15] m.p. 144–146°) and (XV), m.p. 168–170.5° (lit.[15] m.p. 158–161°).

Ring-closure reaction of diols

All intramolecular cyclization reactions were generally carried out as follows. The benzene solution of diols was shaken with a 2*N* solution of HCl for 20–30 min in a separating funnel. The organic layer was washed with water, dried over Na_2SO_4 and then evaporated. The residue was chromatographed to enable separation into each product.

7-Oxa[3]ferrocenophane (IX). The product was recrystallized from hexane to give orange-yellow plates [39% conversion from (IV)], m.p. 147–148° (lit.[4] m.p. 148°).

6,8-Dimethyl-7-oxa[3]*ferrocenophane* (*X*). (*a*). The crude ether obtained from a mixture of the diol (V) (1.0 g) of m.p. 69–70° was chromatographed with a hexane/benzene mixture as the eluant giving separation into two ether bands (first, 0.24 g, 26%; and second, 0.14 g, 15%). Recrystallization of the first band gave orange-yellow plates, m.p. 108.5–109° [(Xa): *trans* form]. (Found: C, 65.83; H, 6.01. $C_{14}H_{16}FeO$ calcd. C, 65.65; H, 6.30%.) IR spectrum (cm^{-1}): 1374 [$\delta(CH_3)$], 1069 [ν(C–O–C)], and 810 [δ(CH) of Cp].

On recrystallization of the second ether band, orange-yellow plates, m.p. 107.5–108° [(Xb): *cis* form] were obtained. (Found: C, 65.85; H, 6.01. $C_{14}H_{16}FeO$ calcd. C, 65.65; H, 6.30%.) IR spectrum (cm^{-1}): 1372 [$\delta(CH_3)$], 1071 [ν(C–O–C)], and 815 [δ(CH) of Cp].

From the reaction mixture, 0.18 g of the unchanged alcohol was recovered (18%) together with some unknown compounds.

(*b*). Use of the pure *meso*-diol (Va) (200 mg) gave the *trans*-ether (55 mg, 29%) and *cis*-ether (6.2 mg, 3.3%). The amount of diol recovered was 49 mg (25%), the diol was a mixture of the *meso* and racemic isomer in 3/1 ratio. From 200 mg of the pure racemic diol (Vb), 3 mg of the *trans*-ether [(Xa): 1.5%] and 49 mg of the *cis*-ether [(Xb): 26%] were obtained, together with recovered diol as a mixture of the *meso* and racemic forms in 1/3 ratio.

6,8-Diphenyl-7-oxa[3]*ferrocenophane* (*XI*). (*a*). The product obtained from the diol (VI) of m.p. 135–136° (500 mg) was chromatographed using a benzene/hexane mixture as eluant to give two ether bands (first, 30 mg, 6.4%; and second, 70 mg, 14%). The two ether compounds were recrystallized from hexane. The amount of diol recovered was 310 mg (62%). The first ether band recrystallized as yellow fibrous needles, m.p. 197–197.5° [(XIa); *trans* form]. (Found: C, 75.85; H, 5.30. $C_{24}H_{20}FeO$ calcd. C, 75.80; H, 5.30%.) IR spectrum (cm^{-1}): 1599 [ν(C=C) of Ph], 1028–1054 [ν(C–O–C)], and 808 [δ(CH) of Cp].

The second ether band recrystallised as yellow needles, m.p. 194.5–195.5° [(XIb); *cis* form]. (Found: C, 75.98; H, 5.32. $C_{24}H_{20}FeO$ calcd.: C, 75.80; H, 5.30%.) IR spectrum (cm^{-1}): 1599 [ν(C=C) of Ph], 1025–1045 [ν(C–O–C)], and 811 [δ(CH) of Cp].

(*b*). The ethers obtained from the racemic diol (VIb) (50 mg) were 2.2 mg of the *trans*-ether [(XIa); 4.5%] and 20 mg of the *cis*-ether [(XIb); 41%]. The recovered diol was a mixture of the *meso* and racemic isomers in 2/3 ratio.

6-Phenyl-8-methyl-7-oxa[3]*ferrocenophane* (*XII*). (*a*). On chromatography of the products from reaction of the diol (VII), which was a mixture of *erythro* and *threo* isomers (1.00 g), two ether bands were obtained (first, 329 mg, 35%; and second, 280 mg, 29%) both being recrystallized from hexane. Little of the initial diol was recovered. The first ether band was obtained as yellow flakes, m.p. 158–159° [(XIIa); *trans* form]. (Found: C, 71.79; H, 5.61. $C_{19}H_{18}FeO$ calcd. C, 71.72; H, 5.70%.) IR spectrum (cm^{-1}): 1601 [ν(C=C) of Ph], 1374 [$\delta(CH_3)$], 1078 [ν(C–O–C)], and 810 [δ(CH) of Cp].

The second ether band was obtained as yellow plates, m.p. 135–136° [(XIIb); *cis* form]. (Found: C, 72.03; H, 5.69. $C_{19}H_{18}FeO$ calcd.: C, 71.72; H, 5.70%.) IR spectrum (cm^{-1}): 1598 [ν(C=C) of Ph], 1373 ($\delta(CH_3)$], 1074 [ν(C–O–C)], and 806 [δ(CH) of Cp].

(*b*). The ethers obtained from 50 mg of the *erythro*-diol (VIIa) were 27 mg (57%) of the *trans*-ether (XIIa) and 4.0 mg (8.1%) of the *cis*-ether (XIIb) whereas the ethers (XII) obtained from 20 mg of the *threo*-diol (VIIa) were 1.0 mg (5.2%) and 10 mg (52%) respectively of the *trans* and *cis* forms.

6,8-Diisopropyl-7-oxa[3]ferrocenophane (XIII) The cyclization reaction involving the diol (VIII) (5.00 g) gave two ether bands on chromatography (first, 0.806 g, 17%; and second, 1.173 g, 25%). An unknown by-product and unchanged diol (0.572 g) were also obtained. The ethers were recrystallized from EtOH. The first ether band was obtained as orange-yellow prisms, m.p. 89–90° [(XIIIa); *trans* form]. (Found: C, 69.55; H, 7.66. $C_{18}H_{24}FeO$ calcd. C, 69.24; H, 7.75%.) IR spectrum (cm^{-1}): 1381 and 1362 [δ(CH_3) of i-Pr], 1054 and 1039 [ν(C–O–C)], and 807 [δ(CH) of Cp].

The second ether band was obtained as orange-yellow prisms, m.p. 66–67° [(XIIIb); *cis* form]. (Found: C, 69.97; H, 7.86. $C_{18}H_{24}FeO$ calcd.: C, 69.24; H, 7.75%.) IR spectrum (cm^{-1}): 1381 and 1363 [δ(CH_3) of i-Pr], 1052 and 1031 [ν(C–O–C)], and 801 [δ(CH) of Cp].

Reaction of diol (XIV) or (XV) with acid. Treatment of diol (XIV) or (XV) (*endo,endo* isomer) with dilute HCl did not afford the corresponding ether, but enabled conversion, respectively, into the *meso-* or racemic bis(dihydroindenyl)iron (XVI) or (XVII) and cyclic vinylferrocene[16], through dehydration involving two H_2O molecules.

Ring-opening reaction of 7-oxa[3]ferrocenophanes

Acidic alumina used in the reaction was prepared by treating Wako activated alumina with 6*N* HCl. The alumina was then washed with water several times, dried and exposed to the air to allow absorption of some moisture. As a general procedure for the reaction, a benzene solution of the ether was stirred with acidic alumina for 5 days. The alumina-absorbed reactant was eluted with AcOEt and the solution evaporated. The residue was chromatographed to enable separation into each component.

Reaction of 6,8-dimethyl-7-oxa[3]ferrocenophane (X). The diol (V) obtained in 24% yield (52 mg) from 200 mg of the *trans*-ether (Xa) consisted mainly of the *meso*-diol (Va) together with a small amount of the racemic diol (Vb) (*ca.* 10% of all diol obtained), and in addition 105 mg of the unchanged *trans*-ether (53%) and 5 mg of the *cis*-ether [(Xb); 2.5%]. The compounds obtained from 500 mg of the *cis*-ether (Xb) consisted of 200 mg of the racemic diol ((Vb); 37%) which contained the *meso*-diol (Va) as a contaminant, 30 mg of the *trans*-ether (5.6%) and 170 mg of the unchanged *cis*-ether (34%).

Reaction of 6,8-diphenyl-7-oxa[3]ferrocenophane (XI). The diol (VI) (18.5 mg, 5.3%) was formed by reaction of 331 mg of the *trans*-ether (XIa) and consisted of a mixture of the *meso* and racemic isomers [(VIa) and (VIb)] in 2/1 ratio. The unchanged *trans*-ether recovered consisted of 273 mg (83%), and in addition 22.5 mg (6.8%) of the *cis*-ether was obtained. Reaction of 384 mg of the *cis*-ether (XIb) resulted in the formation of 8.5 mg of the *trans*-ether (2.2%) and 303 mg of the unchanged *cis*-ether (79%) was recovered together with the diol (VI) (51 mg, 13%), which consisted of a mixture of the *meso* and racemic isomers in 1/5 ratio.

ACKNOWLEDGEMENTS

The authors are grateful to Mrs. Hirose of the Keio University and to Dr. Suzuki of the Tanabe Seiyaku Co. Ltd., for elemental analyses, and also to Miss Kawana of this laboratory for PMR spectral measurements. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, which is gratefully acknowledged.

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