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UNSYMMETRICALLY DISUBSTITUTED FERROCENES—VII

2,7- AND 2,10-DISUBSTITUTED BIFERROCENYLS[1, 2]

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Abstract—The isomeric 2,7- and 2,10-bis(N,N-dimethylaminomethyl)biferrocenyls have been synthesized. Each of these diamines was transformed into a variety of derivatived and a facile intramolecular cyclization in the 2,7-disubstituted series was observed. Evidence for the conformations of the compounds is discussed.

INTRODUCTION

ALTHOUGH biferrocenyl was first synthesized in 1959[3] the systematic chemistry of substituted biferrocenyls has received little attention. This may be due, in part, to the difficult synthetic approaches to many of these compounds. The usual procedures have involved the electrophilic substitution of biferrocenyl or the coupling reactions of suitably substituted ferrocenes. To date, only the acetylation of biferrocenyl has been reported.[4] Using the conditions[4a] under which ferrocene gave a 71% yield of acetylferrocene all three isomeric monoacetylbiferrocenyls were obtained together with three of the possible 14 isomeric diacetylbiferrocenyls, all in rather low yields. The Ullmann coupling reaction[5] was more satisfactory for the preparation of mono- and di-substituted biferrocenyls as yields were usually good and structural assignments were unambiguous.

As part of an investigation of the chemistry of 1,2-disubstituted ferrocenes[1] we wished to synthesize and examine the stereochemistry and reactivity of some 2,7- and 2,10-disubstituted biferrocenyls.[6] These compounds are of interest since they are geometrically distinct and each form will be capable of exhibiting optical isomerism except for the special case where the 2,10-disubstituted compound bears two similar substituents (I) and a *meso* form will result. If however the substituents are large enough to inhibit free rotation about the bond between the two ferrocene residues then, by analogy with 2,2′-disubstituted biphenyls, optical activity will again be possible. The biferrocenyls (I and II) might also adopt eclipsed, skewed or staggered conformations in the presence of different substitutents.

RESULTS AND DISCUSSION

Recently we have reported the synthesis of 2-(N,N-dimethylaminomethyl)ferroceneboronic acid (III)[7] and we considered that the coupling reactions of this intermediate might provide a convenient route to the required biferrocenyl derivatives. Thus the

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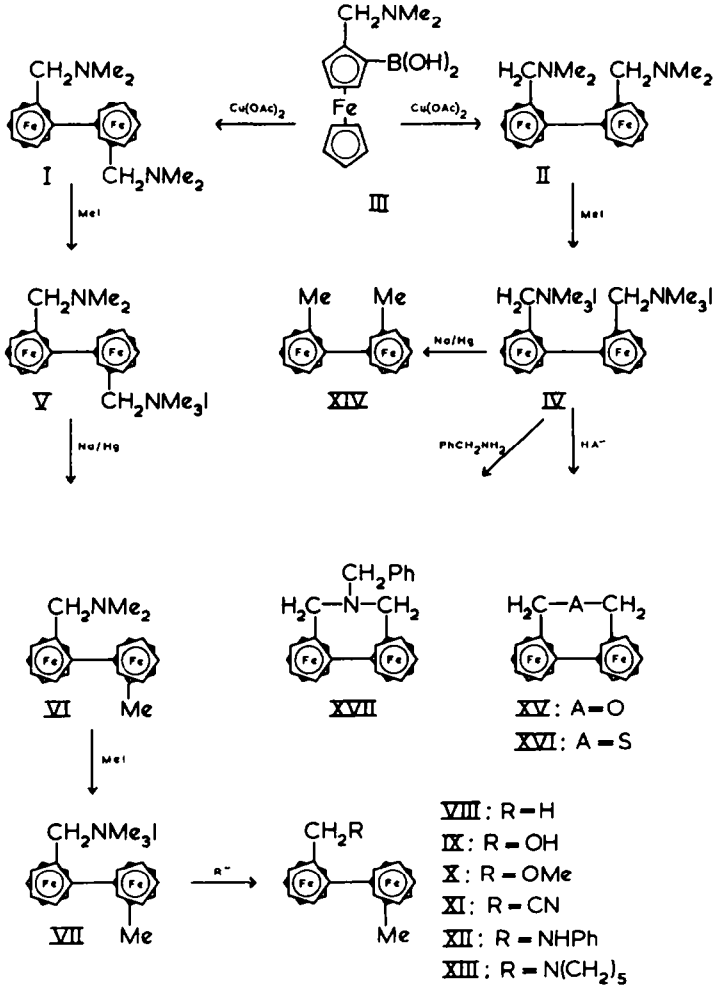
amino acid (III) was converted smoothly by aqueous cupric acetate to a mixture of the two isomeric diamino-biferrocenyls (I and II). These products were conveniently separated by chromatography on alumina and the diamine first eluted formed only the mono-methiodide (V) on treatment with methyl iodide under mild conditions. The more strongly adsorbed diamine gave only the di-methiodide (IV) under similar conditions. The bis-amine (II) has been assigned the unsymmetrical structure since it was resolved into the corresponding enantiomers whilst the bis-amine (I) was not.[8] Also the dimethyl derivative (XIV) was optically active, in contrast to the inactive dimethylbiferrocenyl (VIII).[8]

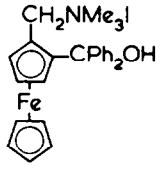


It is noteworthy that 2-(N,N-dimethylaminomethyl)ferroceneacetate was not isolated from the products of the reaction since ferrocenylboronic acid gave predominantly ferrocenylacetate under similar conditions.[9] Similar mixtures of the two diamines (I and II) were obtained from the coupling of 2-lithio(N,N-dimethylamino-

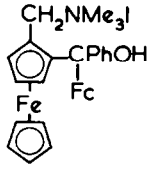
methyl)ferrocene[10] in diethyl ether by anhydrous cobalt chloride,[11] titanium tetrachloride,[12] and copper acetate. Recently Schlogl *et al.*[13] have synthesized the diamines (I and II) by the Ullmann coupling of 2-bromo(N,N-dimethylaminomethyl)ferrocene.

The mono-methiodide (V) was reduced smoothly by sodium amalgam to the methylamine (VI) in high yield and this amine was quarternized by methyl iodide under mild conditions. The quarternary salt (VII) underwent a variety of displacements with C, N and O nucleophilic centres to afford the products VIII–XIII. All of the reactions were complete within 30 min at the reflux temperature.

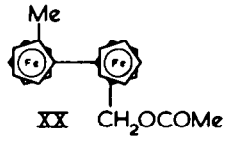
The analogous reactions of the hydroxymethiodide (XVIII)[10, 14] required extended reaction times and this was ascribed to steric impedance of the reactions by the large



XVIII



XIX



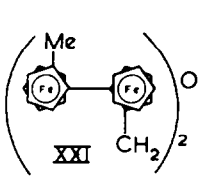
XX

2-substituent. However, any steric effect operating in the biferrocenyl methiodide (VII) must be outweighed by an electronic effect which stabilizes the 2-(ferrocenyl)ferrocene carbonium ion. It is tempting to assign this effect to resonance interaction between the two ferrocenyl residues rather than to an inductive effect but comparison of the present work with other results obtained in this laboratory[15] indicates that resonance plays little part in these reactions. Thus the methiodide (XIX), in which conjugation between the ferrocene nuclei is restricted by the intervening C atom, underwent nucleophilic displacement in less than 30 min at the reflux temperature. These results support the view of Newmeyanov *et al.*[16] that the ferrocenyl group has a very large inductive effect. Further support was provided by the reaction of the biferrocenyl alcohol (IX) with aqueous 2% acetic acid when only the acetate (XX) formed instead of the expected bis(biferrocenyl)ether (XXI).

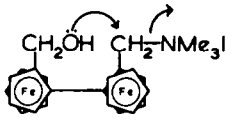
The ester may have been formed by attack of the highly nucleophilic O atom in the alcohol (IX) on the carboxyl C atom of acetic acid. Alternatively the reaction may have involved attack of the 2-ferrocenylferrocene carbonium ion by acetate anions. It is interesting that the methiodide (VII) failed to give the ester (XX) on treatment with aqueous acetic acid. Instead the alcohol (IX) and the bis(biferrocenyl)ether (XXI) were obtained.

Reduction of the dimethiodide (IV) with sodium amalgam gave the expected 2,7-dimethylbiferrocenyl (XIV) isomeric with the biferrocenyl (VIII) a low yield of the cyclic ether (XV) was also obtained. As anticipated, the latter was obtained as the major product from the reaction of the dimethiodide (IV) with aqueous acid or base and the product was presumably formed by a facile intramolecular nucleophilic substitution of the intermediate hydroxy-methiodide as indicated in (XXII). Pauson *et al.*[17] have recently suggested a similar mechanism for the formation of 1,1′-β- oxatrimethyleneferrocene from the basic hydrolysis of 1,1′-bis(N,N-dimethylaminomethyl)ferrocene dimethiodide. The cyclic ether (XV) has also been prepared by the manganese

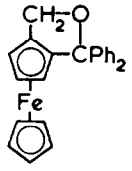
dioxide oxidation of the amine (II).[13] The sulphur (XVI) and nitrogen (XVII) analogues of the cyclic ether (XV) were prepared by nucleophilic substitution of the dimethiodide (IV) by sodium sulphide and benzylamine respectively.



XXI



XXII



XXIII

The stability of the 7-membered ring in the cyclic ether (XV) was demonstrated by its failure to cleave in aqueous-ethanolic acetic acid. These conditions readily opened the 5-membered ring in the ether (XXIII)[18] and this suggests a lowering of the ring strain on increasing the size from 5 to 7 members, as is expected.

UV spectra. In cyclohexane solution biferrocenyl shows absorption maxima at 227, 257 and 303 mμ, the 257 mμ band corresponds to the $\pi \rightarrow \pi^*$ band of ferrocene (220 mμ) bathochromically shifted and increased in intensity by conjugation between the two substituted cyclopentadienyl rings. The UV spectra of the disubstituted biferrocenyls prepared in this study are summarized in the Table. From the Table it may be

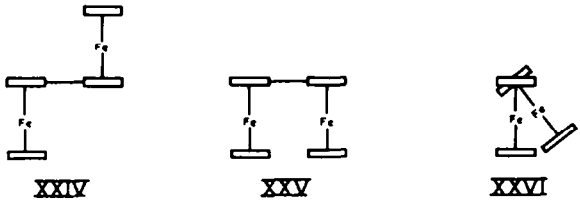
UV ABSORPTIONS OF SOME 2,7- AND 2,10-DISUBSTITUTED BIFERROCENYLS

Compound	Absorption maxima mμ (log ε)			
I	198 (4·65)	222 (4·68)	255* (4·03)	298 (3·88)
VI	196·5 (4·62)	222 (4·69)	255* (4·03)	296 (3·86)
IX	196·5 (4·56)	222 (4·64)	255* (4·01)	295·5 (3·85)
X	196.5 (4·58)	222 (4·66)	255* (4·03)	295·5 (3·85)
VIII	197 (4·56)	222 (4·68)	255* (4·01)	294 (3·85)
XI	196·5 (4·56)	221 (4·64)	255* (4·00)	293·5 (3·80)
XII	199 (4·80)	221·5 (4·67)	—	295 (3·96)
XIII	196·5 (4·65)	221·5 (4·71)	255* (4·05)	295·5 (3·88)
XX	197·5 (4·63)	222 (4·67)	255* (4·01)	295 (3·82)
II	201 (4·77)	215* (4·63)	250* (3·96)	300* (3·31)
XIV	201·5 (4·66)	215* (4·55)	250* (3·88)	300* (3·30)
XV	206 (4·54)	226·5 (4·67)	270* (3·98)	299·5 (3·95)
XVII	202 (4·67)	224·5 (4·70)	257* (4·05)	299·5 (3·92)
XVI	206 (4·57)	225·5 (4·64)	266* (3·97)	301 (3·86)

* shoulder.

seen that the $\pi \rightarrow \pi^*$ band increased in wavelength in the order of substitution of the diferrocenyls: 2,7- < 2,10- < 2,7-cyclic. This order may be rationalized since the 2,7-isomers cannot adopt the staggered conformation (XXIV) without steric interaction between the side chains, or the eclipsed conformation (XXV) without interactions between the unsubstituted cyclopentadienyl rings and may adopt a skewed conformation (XXVI) with some conjugation between the substituted cyclopentadienyl rings.

Thus these isomers show the smallest bathochromic shifts and the weakest conjugation between the disubstituted cyclopentadienyl rings. The sterically preferred conformations of the 2,10-isomers is staggered (XXIV) and conjugation is facilitated in this



XXIV XXV XXVI

form as is indicated by the larger bathochromic shifts observed for these derivatives than for the 2,7-isomers. The heterocyclic 2,7-disubstituted biferrocenyl derivatives (XV, XVI, XVII) are held rigidly in the staggered conformations (XXIV) and show the largest bathochromic shifts of the band confirming the strongest conjugation in this form.

IR spectra. The principal IR absorptions of the compounds prepared in this study are recorded in the Experimental. Each of the disubstituted biferrocenyls contained two unsubstituted cyclopentadienyl rings and showed the expected absorption[20] near to 1100 and 1000 cm^{-1}. The region near to 900 cm^{-1} was not useful in assigning the dispositions of the substituents in the cyclopentadienyl rings.

EXPERIMENTAL

For general directions see Part I.[14] the UV spectra were recorded in cyclohexane.

2,7- *and* 2,10-*Bis*(N,N-*dimethylaminomethyl*)*biferrocenyl* (I *and* II). A soln of cupric acetate monohydrate (4·0 g, 0·02 mole) in water (100 ml) was added to a stirred suspension of III (2·87 g, 0·01 mole) in water (100 ml) and the mixture was heated to 50° for 1 hr. The cooled soln was basified with solid $NaHCO_3$ and then extracted with ether. The dried ($MgSO_4$) ethereal extracts were distilled and the residue was chromatographed on alumina in benzene. Benzene eluted 2,10-*bis*(N,N-*dimethylaminomethyl*)*biferrocenyl* (0·49 g, 21%) which crystallized from ether or light petroleum as orange granular crystals m.p. 203–205·5°. (Found: C, 64·60; H, 6·69; Fe, 23·03; N, 5·85; mol.wt., cryoscopic in benzene, 489. $C_{26}H_{32}Fe_2N_2$ requires: C, 64·49; H, 6·66; Fe, 23·08; N, 5·79%, mol. wt. 484). Principal IR absorption frequencies at 1467m, 1262m, 1105s, 1023s, 1004s, 828s cm^{-1}.

Ether eluted N,N-dimethylaminomethylferrocene (0·97 g) which was identified by its IR spectrum.

Methanol–ether mixtures eluted 2,7-*bis*(N,N-*dimethylaminomethyl*)*biferrocenyl* (0·65 g, 27%) which crystallized from light petroleum as dark orange plates, m.p. 103–105·5°. (Found: C, 64·82; H, 6.77; Fe, 22·65; N, 5·64%; mol.wt., cryscopic in benzene, 477). Principal IR absorption frequencies at 1460s, 1255s, 1170m, 1106s, 1018s, 1000sh, 850s, 820s cm^{-1}.

2,10-*Bis*(N,N-*dimethylaminomethyl*)*biferrocenyl monomethiodide* (V). To a soln of I in the minimum of dry benzene was added an excess MeI, and the soln was left at room temp for 30 min. Addition of dry ether precipitated the *monomethiodide* (V) in quantitative yield, and it crystallized from MeCN on the addition of dry ether as yellow needles which did not melt below 250° but decomposed slowly from 140°. (Found: C, 52·20; H, 5.50; N, 4·58; $C_{27}H_{35}Fe_2IN_2$ requires: C, 51·80; H, 5.64; N, 4·48%). Principal IR absorption frequencies at 1468s, 1420m, 1294m, 1163m, 1106s, 1008s, 888s, 836s cm^{-1}.

Chromatography of the crude product showed that no dimethiodide formation had occurred, even after leaving the reaction mixture at room temp for 2 days.

2-*Methyl*-10-(N,N-*dimethylaminomethyl*)*biferrocenyl* (VI). Water (250 ml) was added to a mixture of V (5·0 g, 0·008 mole) and NaHg (10%; 30·0 g, 0·13 mole), and the flask heated at 130° until the

evolution of Me_3N had ceased (3 hr). The cooled reaction mixture was extracted with ether and the dried ($MgSO_4$) ethereal extracts were distilled to leave an orange solid which was dissolved in benzene and chromatographed on neutral alumina. Ether eluted the *product* VI (2·9 g, 82%) which crystallized from light petroleum as dark orange plates, m.p. 126–128·5°. (Found: C, 65·48; H, 6·21; Fe, 25·22; N, 3·16. $C_{24}H_{27}Fe_2N$ requires: C, 65·34; H, 6·17; Fe, 25·33; N, 3·18%). Principal IR absorptions frequencies at 1460s, 1402m, 1258s, 1176s, 1104s, 1038s, 1016s, 826s cm^{-1}.

The methiodide (VII) was prepared in dry benzene as described above, and was precipitated as a yellow powder by addition of dry ether. It crystallized from MeCN–dry Et_2O as a yellow microcrystalline solid that did not melt below 230° but darkened from 165°. (Found: C, 51·73; H, 5·27; Fe, 18·93; N, 2·50. $C_{25}H_{30}Fe_2IN$ requires: C, 51·49; H, 5·19; Fe, 19·15; N, 2·40%). Principal IR absorption frequencies at 1484s, 1420m, 1384m, 1112s, 1010m, 890s, 830s cm^{-1}.

2-Methyl-10-(hydroxymethyl)biferrocenyl (IX). A suspension of VII (1·0 g, 0·0017 mole) in NaOH aq (50 ml, 0·5M) was heated to reflux until the evolution of Me_3N had ceased (30 min). The reaction mixture was cooled and then extracted with ether. The dried ($MgSO_4$) ethereal extracts were distilled and the residue was chromatographed on neutral alumina. The *alcohol* IX (0·58 g, 82%) was eluted with ether–benzene mixtures, and it crystallized from ether–light petroleum as orange granular crystals, m.p. 184–195°. (Found: C, 63·83; H, 5.37; Fe, 27·20; O, 4.01. $C_{22}H_{22}Fe_2O$ requires: C, 63·81; H, 5.36; Fe, 27·08; O, 3·8%). Principal IR absorption frequencies at 3450s, 1415m, 1224m, 1110s, 1010s, 840s, 820s cm^{-1}.

2-Methyl-10-(Methoxymethyl)biferrocenyl (X). A reaction of VII (0·80 g, 0·00137 mole) in a mixture of NaOH aq (30 ml, 0·8M) and MeOH (12 ml) was carried out as described in the preceding experiment; reflux was maintained for 30 min. The *methyl ether* X (0·28g, 49%) was eluted from neutral alumina by benzene–light petroleum mixtures and was crystallized from ether–light petroleum as dark orange plates, m.p. 123·5–125·5°. (Found: C, 64·35; H, 5·64; Fe, 26·07; O, 3·90. $C_{23}H_{24}Fe_2O$ requires: C, 64·52; H, 5·65; Fe, 26·10; , 3·74%). Principal IR absorption frequencies at 1458m, 1236m, 1118s, 1090s, 1016s, 915m, 848s, 830s cm^{-1}.

Benzene–ether mixtures eluted XI (0·20 g, 35%), identified by its m.p. and IR spectrum.

2,10-Dimethylbiferrocenyl (VIII). A reaction between VII (1·0 g, 0·0017 mole) and NaHg (10%: 5.0 g, 0·022 mole) in water (50 ml) was carried out as previously described; reflux was continued for 30 min. The *product* VIII (0·15 g, 22%) was eluted from neutral alumina by light petroleum and it crystallized from the same solvent as orange plates, m.p. 158–159°. (Found: C, 66·21; H, 5·64; Fe, 27·88. $C_{22}H_{22}Fe_2$ requires: C, 66·37; H, 5·57; Fe, 28·06%). Principal IR absorption frequencies at 1445m, 1380s, 1230m, 1140m, 1110s, 930m, 830s, 820s cm^{-1}.

Benzene–ether mixtures eluted IX (0·42 g, 59%).

2-Methyl-10-(cyanomethyl)biferrocenyl (XI). A reaction of VII (0·40 g, 0·00068 mole) with KCN (1·0 g, 0·015 mole) in water (30 ml) was carried out as described in the preceding experiment; reflux was continued for 30 min. The *cyanide* XI (0·14 g, 48%) was eluted from neutral alumina by benzene and crystallized from ether–light petroleum as orange needles, m.p. 149–151° (dec). The compound partly decomposed whilst on the alumina column. (Found: C, 65·44; H, 4·99; Fe, 26·36; N, 3·27. $C_{23}H_{21}Fe_2N$ requires: C, 65·29, H, 5·00; Fe, 26.41; N, 3·31%). Principal IR absorption frequencies at 2270m, 1420s, 1110s, 1014s, 840s, 818s cm^{-1}.

2-Methyl-10-(N-anilinomethyl)biferrocenyl (XII). A reaction between VII (0·80 g, 0·00137 mole) and aniline (1·0 g, 0·011 mole) in water (30 ml) was carried out as described above, reflux being maintained for 30 min. The *product* XII (0·62 g, 92%) was eluted from neutral alumina by light petroleum and it crystallized from ether–light petroleum as dark orange granular crystals, m.p. 122·5–124°. (Found: C, 69·00; H, 5·32; Fe, 23·01; N, 2·87. $C_{28}H_{27}Fe_2N$ requires: C, 68·74; H, 5·57; Fe, 22·84; N, 2·86%). Principal IR absorption frequencies at 3370s, 1600s, 1510s, 1320s, 1104m, 1012s, 1000sh, 764s, 704s cm^{-1}.

2-Methyl-10-(N-piperidinomethyl)biferrocenyl (XIII). A reaction of VII (0·60 g, 0·0010 mole) with piperidine (2 ml) in water (30 ml) was carried out as described above; reflux was continued for 30 min. Benzene–ether mixtures eluted the *tertiary-amine* XIII (0·44 g, 89%) from neutral alumina as an orange oil which crystallized from ether–light petroleum as golden yellow needles, m.p. 142·5–144°. (Found: C, 67·25; H, 6·44; Fe, 23·08; N, 2·99. $C_{27}H_{31}Fe_2N$ requires: C, 67·39; H, 6·50; Fe, 23·22; N, 2·91%). Principal IR absorption frequencies at 2920s, 1460s, 1344s, 1272m, 1108s, 1042s, 1010s, 830s cm^{-1}.

Bis[2-methyl(10-methylbiferrocenyl)] ether (XXI). A suspension of VII (0·58g, 0·001 mole) in 5% aqueous AcOH (20 ml) was heated to reflux for 30 min. The cooled reaction mixture was diluted with a

large volume of water and then extracted with ether. The dried ($MgSO_4$) ethereal extracts were distilled and the residue was chromatographed on neutral alumina in benzene. The *ether* XXI (0·25 g, 62%) was eluted by benzene–light petroleum mixtures and crystallized from ether–light petroleum as a yellow microcrystalline solid, m.p. 181°. (Found: C, 65·43; H, 5·21; $C_{44}H_{42}Fe_4O$ requires: C, 65·22; H, 5·23%). Principal IR absorption frequencies at 1455m, 1382m, 1110s, 1052s, 1012s, 822s cm^{-1}.

Ether eluted IX (0·13 g, 31%), identified by its IR spectrum and m.p.

2-*Methyl*-10-*(acetoxymethyl)biferrocenyl* (XX). The alcohol IX (0·28g, 0·00068 mole) was added to 2% aqueous AcOH (50 ml) and the mixture was boiled under reflux for 15 hr. The cooled reaction mixture was extracted with ether and the dried ethereal extracts were distilled. The residue was dissolved in benzene and chromatographed on neutral alumina. Benzene–light petroleum mixtures eluted 2-*methyl*-10-*(acetoxymethyl)biferrocenyl* XX (0·072 g, 23%) which crystallized from ether–light petroleum as orange-red needles, m.p.170–171°. (Found: C, 63·65; H, 5·52; Fe, 24·59. $C_{24}H_{24}Fe_2O_2$ requires: C, 63·19; H, 5·31; Fe, 24·49%). Principal IR absorption frequencies 1728s, 1456s, 1380s, 1230s, 1112s, 1008s, 938s, 822s cm^{-1}.

Ether eluted the starting alcohol (0·15 g).

2,7-*Bis*(N,N-*dimethylaminomethyl)biferrocenyl dimethiodide* (IV). To a soln of II in MeCN was added an excess MeI, and the soln was left at room temp for 5 min. Addition of dry ether precipitated the *dimethiodide* IV in quantitative yield as a yellow microcrystalline solid which did not melt below 250° but darkened from 175°. (Found: C, 42·46; H, 5·04; Fe, 14·02; N, 3·47. $C_{28}H_{38}Fe_2I_2N_2$ requires: C, 43·79; H, 4·99; Fe, 14·54; N, 3·65%). Principal IR absorption frequencies at 1488s, 1382s, 1110s, 1092s, 1010s, 890s, 828s cm^{-1}.

2,7-*Dimethylbiferrocenyl* (XIV). Water (50 ml) was added to a mixture of IV (2·0 g, 0·0026 mole) and NaHg (10%; 20g, 0·087 mole) and the whole was heated under reflux for 2 hr. The cooled reaction mixture was extracted with ether and the ethereal extracts were dried ($MgSO_4$). The ether was distilled off and the residue was placed on a column of neutral alumina in benzene–light petroleum. 2,7-*Dimethylbiferrocenyl* XIV (0·36 g, 35%) was eluted by light petroleum and crystallized from the same solvent as light orange needles, m.p. 90·5°. (Found: C, 66·27; H, 5·56; Fe, 28·01. $C_{22}H_{22}Fe_2$ requires: C, 66·37; H, 5·57; Fe, 28·06%). Principal IR absorption frequencies at 1455m, 1420m, 1379m, 1152m, 1112s, 1068m, 1009s, 822s, 698m cm^{-1}.

Benzene eluted 2,7-(β-*oxatrimethylene)biferrocenyl* XV (0·07 g, 6·5%) which crystallized from ether–light petroleum as orange-brown needles, m.p. 164–165·5°. (Found: C, 64·44; H, 4·97; Fe, 27·03; O, 3·83; mol.wt. by measurement of vapour pressure, 402. $C_{22}H_{20}Fe_2O$ requires: C, 64·12; H, 4.89; Fe, 27·11; O, 3·88; mol. wt. 412). Principal IR absorption frequencies at 1460m, 1410m, 1212m, 1104s, 1035m, 1006s, 932m, 828s cm^{-1}.

2,7-(β-*Oxatrimethylene)biferrocenyl* (XV). (a) The dimethiodide IV (2.00 g, 0·0026 mole) was added to NaOH aq (50 ml, 1M) and the stirred mixture was boiled under reflux for 5 hr. After the usual work-up, the residue was dissolved in benzene and chromatographed on neutral alumina. Elution with benzene–light petroleum mixtures afforded the *ether* XV (0·58 g, 54%), identical (m.p. and IR spectrum) with the minor product obtained from the reaction of IV with NaHg.

(b) The dimethiodide IV (2·58 g, 0·0034 mole) was reacted with 15% aqueous AcOH (145 ml) at the reflux temp for 90 min. The cooled reaction mixture was extracted with ether after being diluted with a large volume of water, and the dried ethereal extracts were distilled. Chromatography of the residue on neutral alumina yield the *ether* XV (1·01 g, 77%) which was identified by its IR spectrum and m.p.

2,7-[β-(*Benzylaza)trimethylene]biferrocenyl* (XVII). A reaction between IV (0·80 g, 0·0010 mole) and benzylamine (2 ml) in water (25 ml) was carried out as described in the preceding experiment; reflux was maintained for 5 hr. The *product* XVII (0·41 g, 79%) was eluted from neutral alumina by benzene–light petroleum mixtures as an orange solid that decomposed slowly in organic solvents. It was crystallized from a saturated soln in light petroleum at 0° to afford yellow feathery crystals, m.p. 141.5°. (Found: C, 69·60; H, 5·66; Fe, 22·26; $C_{29}H_{27}Fe_2N$ requires: C, 69·49; H, 5·43; Fe, 22·29%). Principal IR absorption frequencies at 1460m, 1378m, 1322m, 1108s, 1010s, 830s, 752s, 706m cm^{-1}.

2,7-(β-*Thiatrimethylene)biferrocenyl* (XVI). A reaction of IV (0·80 g, 0·0010 mole) with $Na_2S.9H_2O$ (2.0 g, 0·008 mole) in water (25 ml) was carried out as described in the preceding experiment; reflux was continued for 5 hr. The *product* XVI (0·22 g, 50%) was eluted from neutral alumina by benzene–light petroleum mixtures and crystallized from ether–light petroleum at 0° as orange needles, m.p. 144–146°. (Found: C, 61·88; H, 4.65; Fe, 26·10; S, 7·58; $C_{22}H_{20}Fe_2S$ requires: C, 61·71; H, 4·71; Fe, 26·10; S, 7·49%). Principal IR absorption frequencies at 1412s, 1200m, 1102s, 1035m, 1002s, 830s cm^{-1}.

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