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SYNTHESIS AND STEREOCHEMISTRY OF *CIS*- AND *TRANS*-2,5-DIFERROCENYLTETRAHYDROFURAN*

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Abstract—Reduction of 1,2-diferrocenoylethane (I) with LAH gave a diol (II), which was converted to 2,5-diferrocenyltetrahydrofuran (III) by polyphosphoric acid or 10% sulphuric acid. *cis* and *trans* Stereoisomers of III were separated; *trans*-isomer IIIa, m.p. 146–147°, and *cis*-isomer IIIb, m.p. 124–125°, in 1:8 ratio. The configuration of IIIa and IIIb was assumed from their NMR spectra and reductive cyclization reaction mechanism. The structure of the *cis*-isomer IIIb was established by the catalytic reduction of 2,5-diferrocenylfuran (IV), which was prepared from I by treatment with polyphosphoric acid or conc sulphuric acid. Catalytic reduction of IV by Raney nickel or platinum oxide resulted in hydrogenolysis, and 1,4-diferrocenylbutane (V) was formed, together with small amounts of ethylferrocene (VI), which was identified by the Clemmensen–Martin reduction of I.

RECENTLY, Sugiyama *et al.*[1] reported the synthesis of 2,5-diferrocenyltetrahydrofuran from 1,2-diferrocenoylethane by reductive intramolecular cyclization. The present investigation was undertaken because of interest in the stereochemical course of formation of tetrahydrofruan ring and the conformation of the *cis*- and *trans*-stereoisomers of 2,5-diferrocenyltetrahydrofuran.

RESULTS AND DISCUSSION

Reduction of 1,2-diferrocenoylethane (I) with LAH gave quantitatively a diol (II), m.p. 136–137°, together with a small amount of probably its stereoisomer the purification of which failed. The diol II may exist as the stereoisomers of *racemic* and *meso* forms. The present diol II was repeatedly purified by column chromatography and recrystallization, but its IR and NMR spectra did not change, and also it gave one spot at R_f 0·23 (benzene : EtOH = 30 : 1) in TLC.[2] The diol II was assumed to have a *racemic*-configuration from its NMR spectrum and reduction mechanism, which will be discussed later. The benzene solution of II was passed through a column of alumina or treated with sulphuric acid, and fractional crystallization from ethanol gave two cyclic ethers. The minor product first crystallized as a golden-yellow plates, m.p. 146–147° (IIIa), and the major product crystallized, after standing a few days, as yellow-brown prisms, m.p. 126–127° (IIIb). The ratio of IIIa to IIIb was about 1:8. Compounds IIIa and IIIb are *trans*- and *cis*- stereoisomers of 2,5-diferrocenyltetrahydrofuran, which was determined by elemental analyses, and from IR and NMR spectra which are shown in Figs 1 and 2, respectively.

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* Organometallic Compounds. VII. Part VI. K. Yamakawa and M. Hisatome, *Tetrahedron Letters* No. 29, 2827 (1967).

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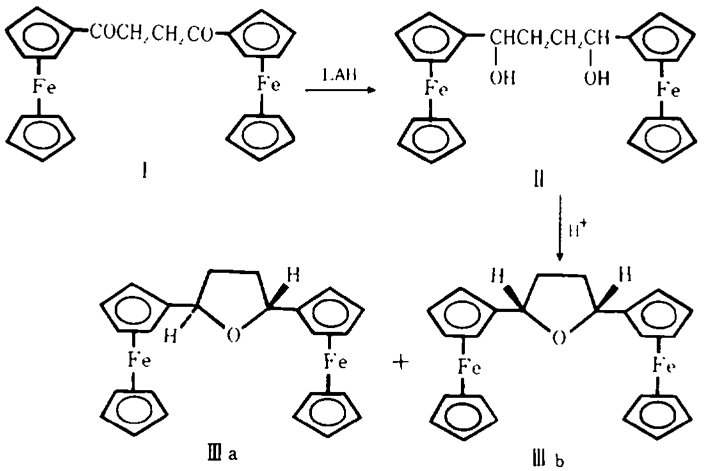
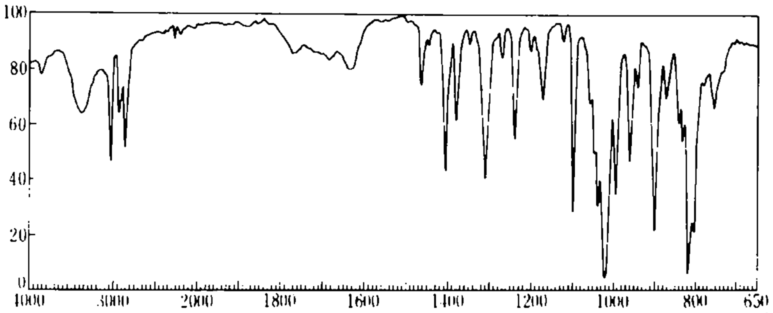
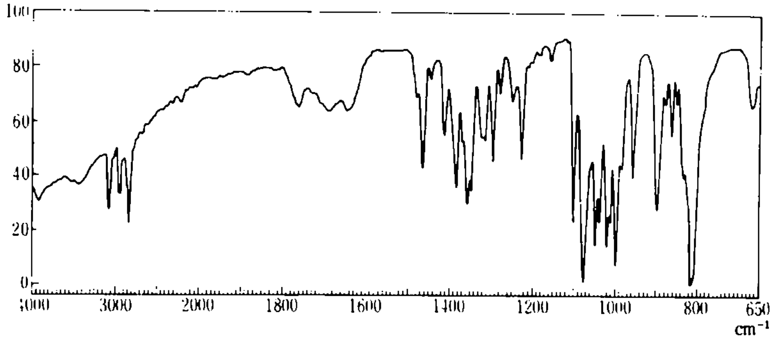
CHART 1



It is not clear whether the conformation of 2,5-diferrocenyltetrahydrofuran is a half-chair (C_2) or an envelope (Cs) form. If the half-chair form is more stable, as has been indicated[3] for some 5-membered heterocyclic compound, the conformations of



trans-IIIa



cis-IIIb

FIG. 1 IR spectra of the isomeric 2,5-diferrocenyltetrahydrofurans.

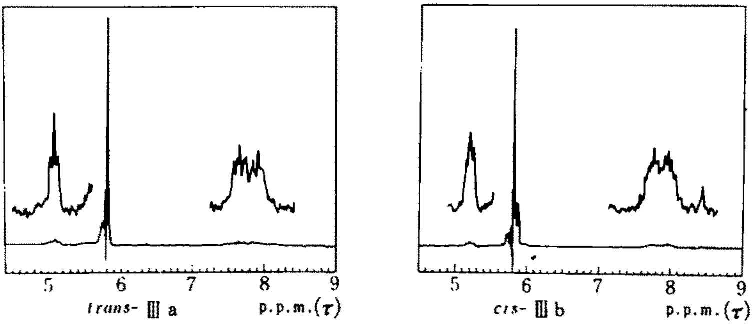


FIG. 2 NMR spectra of the stereoisomeric 2,5-diferrocenyltetrahydrofurans.

the *cis*- and *trans*-isomers in half-chair form **1** and **2** will be as shown in Fig. 3a The envelope form, however, should also be taken into consideration, since the transformation from the half-chair to the envelope form is known to take place easily through *pseudo*-rotation in tetrahydrofuran.[4] The conformations (**3**–**6**) of the isomers in the envelope form are summarized in Fig. 3b. The true situation may be defined as an equilibrium mixture of all these conformations **1** to **6**. The very bulky ferrocenyl group is likely to take the equatorial configuration relative to the tetrahydrofuran ring.

The *cis*- configuration may most favor the envelope (Cs) form **4**, because the two ferrocenyl groups have quasi-diequatorial bond and the ring inversion is prevented

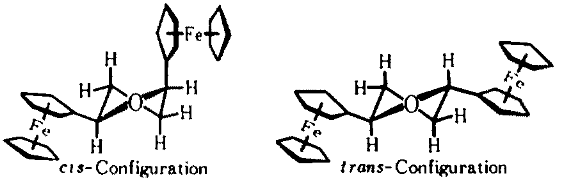


FIG. 3a Conformational isomers of 2,5-diferrocenyltetrahydrofurans in half-chair forms.

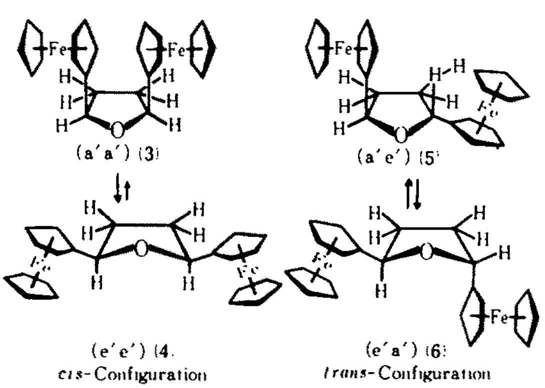


FIG. 3b Conformational isomers of 2,5-diferrocenyltetrahydrofurans in envelope forms

due to the quasi-diaxial bond of the ferrocenyl group. On the contrary, the *trans*-configuration may most favor the half-chair (C_2) form **2**, because the bulky ferrocenyl groups have a more stable quasi-diequatorial configuration in half-chair form than quasi-axial-equatorial configuration in envelope form (**5** and **6**).

The stereochemistry of IIIa and IIIb of 2,5-diferrocenyltetrahydrofuran will be discussed on the basis of their IR and NMR spectra, and from their stereochemical reaction mechanism.

The IR spectra of 2,5-diferrocenyltetrahydrofurans (IIIa and IIIb); Fig. 1) show a characteristic difference for the ether band at 1076 and 1023 cm^{-1}, which can be used for the differentiation and the identification between the *cis*- and *trans*-isomers.

The NMR spectra of 2,5-diferrocenyltetrahydrofuran (IIIa and IIIb) show signals of considerable complexity (Fig. 2). The spectra of IIIa and IIIb appeared with the following τ values of chemical shifts: For IIIa, m.p. 146–147°; β-protons of C_3 and C_4 at 8·0–7·5, cyclopentadienyl ring protons appeared at 5·81, and α-protons of C_2 and C_5 centered at 5·10. For IIIb, m.p. 126–127°; β-protons of C_3 and C_4 at 8·1–7·6, cyclopentadienyl ring protons appeared at 5·81, and α-protons of C_2 and C_5 centred at 5·20; $\Delta\delta$ = IIIa (α-H) – IIIb (α-H) = 0·10 ppm or 6 c/s. The signals of the α-protons are displaced lower field in the *trans*-isomer (IIIa) which are more equatorial protons compared with the *cis*-isomer ones (IIIb). It is due in the main to bond anisotropic effect by C-3—C-4 bond of the tetrahydrofuran rings in the most stable conformation (**2** and **4**),* while it seems anisotropy of ferrocenyl ring contributes in nearly equal degree to α-protons of C_2 and C_5 due to free rotation of the rings. It has been established for 6-membered ring systems that equatorial ring protons absorb at lower field (their experimental disparity lie in the ring 0·1–0·7 ppm) than do their epimeric axial counterparts.[5]

Recently, similar results were observed by Mihailovic *et al.*[6] in NMR spectra of *cis*- and *trans*-2,5-dialkyltetrahydrofuran in their α-protons of C_2 and C_5 about $\Delta\delta$ 0·20–0·10 ppm or 12–6 c/s.

We will now discuss the intramolecular reductive cyclization reaction mechanism of 1,2-diferrocenoylethane (I), and the conformation of the *cis*- and *trans*-2,5-diferrocenyltetrahydrofuran (IIIb and IIIa).

The starting material, 1,2-diferrocenoylethane (I) may exist in the two conformers of *cisoid* and *transoid* forms. In this compound, the planer cyclopentadienyl rings neighbouring the CO group take a skew conformation with respect to ethane linkage. These compounds are in equilibrium between *cisoid* and *transoid* forms, and the latter may be a more favored conformation due to the CO–CO repulsion.

Reduction of the diketone (I) with sodium borohydride gave the diol II, in stereoisomeric *racemic* and *meso* forms. If the compound I has more stable *transoid* conformation (**7**), metal hydride or metal catalyst would approach the CO group by means of stereospecific one-side addition, resulting the formation of a *racemic* diol (**9**).

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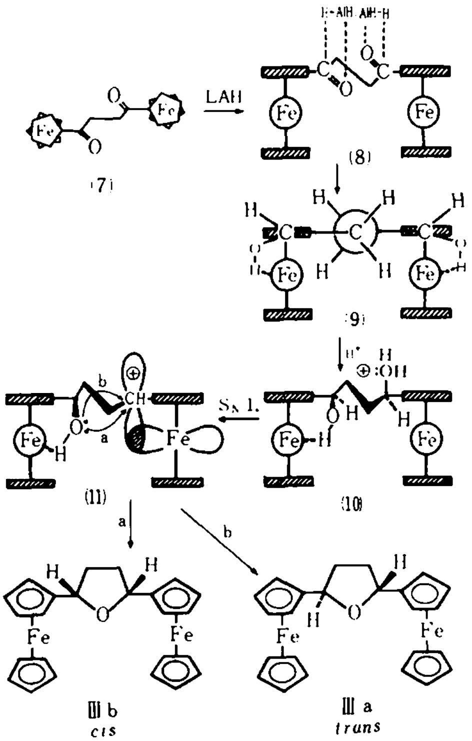
* If for diamagnetic susceptibility value of C—C single bond $-5{\cdot}5 \times 10^{-30}$ cm^3 is used, the difference δ-value can be calculated about 0·1 ppm using the McConnells' equation[5] under the condition for *trans*; $\theta = 44°$, $r = 2{\cdot}7$ Å and for *cis*; $\theta = 63°$, $r = 2{\cdot}4$ Å in the conformation of half-chair (**2**) and envelope (**4**), respectively. This is in good agreement with actual experimental value of 0·1 ppm. This consideration seems to be supported with the fact that the difference of chemical shift between the α-protons in the *trans*- and *cis*-2,5-diphenyltetrahydrofuran was 0·2 ppm by our unpublished data.

Recently, Inamura[7] reported similar results on the reduction of 1,2-dibenzoylethane with metal hydride or metal catalyst which gave a *racemic* diol predominantly.

Acid-catalyst S_N 1 solvolysis of the diol II would proceed through an intermediate carbonium ion (**11**) dehydration. The α-ferrocenylcarbonium ion is known to be in unusual stabilization with a participation of bonded iron atom orbital, which was found by Cais *et al.*[8] for various ferrocenylcarbonium ions. Hill and Richards[9] found that S_N 1 solvolysis of *pseudo-exo-* and *pseudo-endo*-α-ferrocenylcarbinyl acetates proceeds in a stereospecific fashion.

It is considered that the solvolysis of the *racemic* diol (**9**) produced an intermediate carbonium ion (**11**) and a more favored S_N i back side attack (course *a*) might have occurred predominantly leading to the *cis*-configuration of tetrahydrofuran in IIIb. In our experiment, the diketone (I) was reduced with LAH and the complex was decomposed with acid, from which a mixture of tetrahydrofuran derivatives, IIIb, m.p. 126–127°, and IIIa, m.p. 146–147°, were obtained in the ratio of 8:1.

CHART 2



In order to secure the actual proof for the above assumption of configuration of 2,5-diferrocenyltetrahydrofuran (IIIa and IIIb), catalytic reduction for the corresponding furan derivative was attempted. It is generally known that a *cis* addition with hydrogen occurs on catalytic reduction of a substituted furan ring.

For this purpose, the synthesis of 2,5-diferrocenylfuran (IV) was attempted from 1,2-diferrocenoylethane (I). It was reported that 1,2-dibenzoylethane is easily converted to 2,5-diphenylfuran by means of concentrated sulphuric acid,[10] polyphosphoric acid,[11] acetic anhydride-zinc chloride,[12] or DMSO[13]. The diketone (I) was treated with conc sulphuric acid, acetic anhydride–zinc chloride, or DMSO under the conditions for the benzene analogue, but only a tarry product was obtained. Dehydration to furan ring formation seems to be difficult due to the immediate formation of ferricinium ion. However, I was treated with conc sulphuric acid for a prolonged period (3 hr) at room temperature to afford 2,5-diferrocenylfuran (IV) as brown plates, m.p. 187–189°, in a low yield. When I was also treated with polyphosphoric acid at 130–140° or above 70°, as in the case of the benzene analogue, the furan derivative IV was not formed. In this reaction a violet colour developed immediately due to the ferricinium ion and only a polymerized tarry product was obtained. However, under a milder condition as with polyphosphoric acid for 7 hr at 45–47° or at room temperature on standing over-night, a furan derivative (IV) was obtained in 24 and 10% yield, respectively.

The structure of 2,5-diferrocenylfuran (IV) was established by elemental analysis, and Erlich test[14] of brown colour. The IR spectrum of IV shows the characteristic furan band[15] at 1584, 1013, and 776 cm^{-1}, and the NMR spectrum of IV shows the τ value at 3·81 (singlet), which is characteristic of furan derivatives.[16] The UV spectrum of IV shows λ_{max} (EtOH) at 226, 281, 323, and 449 mμ with log ε of 2·34, 3·98, 4·81 and 4·59, respectively.

Catalytic reduction of IV was carried out under various conditions. Moderate conditions at 1, 40, and 60 atm/cm^2 for 10 hr with the Adams catalyst resulted in the recovery of the starting material (IV), but under a stronger conditions, hydrogenolysis together with a bond cleavage occurred. The main product, m.p. 107–108°, was identified as 1,4-diferrocenylbutane (V), which was prepared from the diketone (I) by the Clemmensen-Martin reduction.[17] A minor product as a red viscous oil was identified as ethylferrocene (VI) by elemental analysis and NMR spectrum. The NMR spectrum of VI revealed three Me protons of at 8·81 τ (triplet), two methylene protons at 7·62 τ (quartet), and ferrocene ring protons at 5·92 and 5·88 τ. These results show that the C—C bond rapture occurs between C-3 and C-4 of the furan ring in IV by the hydrogenolysis[18] or Clemmensen–Martin reduction of I.

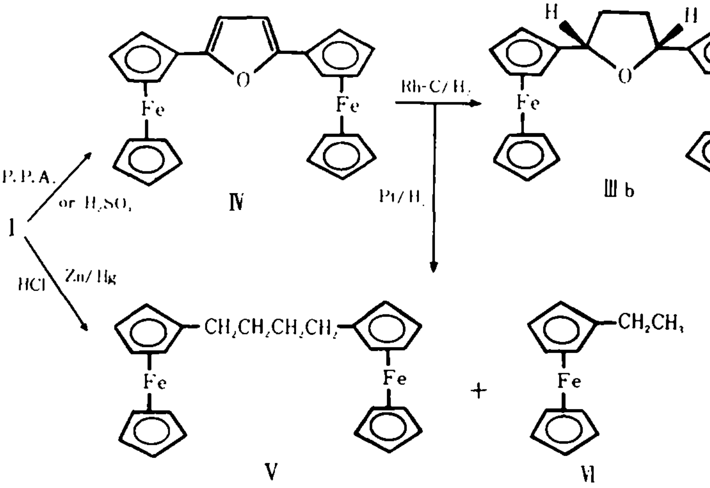
The second reduction in the presence of a Raney nickel catalyst was carried out under various conditions (Experimental). Very strong activated nickel catalyst was used at 130 atm/cm^2 at room temperature, 50° and 110°. All these conditions gave butane derivative (V) of hydrogenolysis product, but reduction at an ice-cold temperature at 130 atm/cm^2 for 8 hr ended in the recovery of the starting material (IV) in 50% yield. However, when deactivated Raney nickel W-2 catalyst was used at 110 atm/cm^2 for 4 hr at room temperature and the reaction mixture was chromatographed with benzene, the starting material (IV) was recovered in 75% yield. The second eluate of R_f 0·25, m.p. 126–127°, was identified as one of the possible isomers, *cis*-2,5-diferrocenyltetrahydrofuran (IIIb) by mixed m.p. of 126–127° and by IR comparison.

The third reduction with 5% rhodium–charcoal catalyst was carried out with hydrogen at an ordinary pressure for 2 hr at room temperature and gave a quantitative amount of *cis*-tetrahydrofuran derivative (IIIb), m.p. 126–127°, which was

identified as *cis*-2,5-diferrocenyltetrahydrofuran (IIIb). Reduction with 5% rhodium-charcoal catalyst at 60 atm/cm^2 for 6 hr at room temperature gave a mixture of 1,4-diferrocenylbutane (V) and tetrahydrofuran derivative (IIIb) in the 15:1 ratio.

From these results, the assignment of *cis*- and *trans*-configuration to 2,5-diferrocenyltetrahydrofuran was established as *cis* for IIIb, m.p. 126–127°, and *trans* for IIIa, m.p. 147–149°.

CHART 3



EXPERIMENTAL

All m.ps are uncorrected. IR spectra were measured for KBr pellet with Hitachi EPI-2 spectrophotometer. NMR spectra were determined in $CDCl_3$ with a Varian A-60 spectrometer, using TMS as internal reference. Microanalyses were by Mrs. K. Hirose, Keio University, Tokyo.

1,2-*Diferrocenoylethane* (I)

Compound I prepared by the modification of the procedure described,[1] gave orange needles, m.p. 186–187° (reported[1] m.p. 185–186°), 34% yield. (Found: C, 63·79; H, 5·03. $C_{24}H_{22}O_2Fe$ requires: C, 63·44; H, 4·85%); IR spectrum (KBr): 1674 cm^{-1} (C=O). NMR ($CDCl_3$) τ: 6·81 (methylene), 5·70 (s*, cyclopentadienyl ring), 5·47 (tr, J = 3 c/s, α-protons of ring), 5·52 (tr, J = 3 c/s, β-protons of ring).

1,4-*Dihydroxy*-1,4-*diferrocenylbutane* (II)

A soln of I (0·50 g) in anhyd THF (25 ml) and EtOH (1:1) was gradually added to a stirred slurry of LAH (0·20 g) in anhyd THF (25 ml). The mixture was stirred for 2 hr at room temp. Excess hydride was decomposed with EtOAc (20 ml) and ether (30 ml). The organic layer was washed with H_2O and dried. After evorporation of the solvent, 0·48 g (95·5%) of crude solid, m.p. 134–135°, was obtained, which was recrystallized from EtOH as yellow needles (II; 0·42 g), m.p. 136–137° (reported[1] m.p. 134–135°). (Found: C, 62·88; H, 5·63. $C_{24}H_{26}O_2Fe_2$ requires: C, 62·88; H, 5·68%). IR spectrum (KBr): 3480 cm^{-1} (OH); NMR ($CDCl_3$) τ: 8·22 (methylene protons), 7·81 (methine protons), and 5·85 (s, cyclopentadienyl ring).

trans- *and* cis-2,5-*Diferrocenyltetrahydrofuran* (IIIa *and* IIIb)

A soln of II (1·5 g) in benzene (100 ml) was shaken with 10% H_2SO_4 (50 ml) for 2 hr at room temp. The benzene layer was separated and washed with H_2O. Removal of the solvent afforded a solid (1·4 g), m.p.

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* s = singlet; tr = triplet; qu = quartet; m = multiplet.

110–120° which was dissolved in benzene and chromatographed on alumina. The eluate was fractionally crystallized from EtOH yielding *trans*-IIIa (0·1 g) as yellow plates, m.p. 146–147°. (Found: C, 65·34; H, 5·59. $C_{24}H_{24}OFe_2$ requires: C, 65·45; H, 5·45%). IR spectrum (KBr): 1023 cm^{-1} (cyclic ether). NMR spectrum ($CDCl_3$) τ: 7·80 (m, methylene protons), 5·81 (s, cyclopentadienyl ring), and 5·20 (tr; J = 5 c/s, α-methine protons).

After a few days the second crop of crystals separated from the above mother soln, affording *cis*-IIIb (0·75 g) as orange-red prisms, m.p. 126–127° (reported[1] m.p. 124·5–125°). (Found: C, 65·21; H, 5·17. $C_{24}H_{24}OFe_2$ requires: C, 65·45; H, 5·45%); IR spectrum (KBr): 1076 cm^{-1} (cyclic ether). NMR spectrum ($CDCl_3$) τ: 7·85 (m, methylene protons), 5·81 (s, cyclopentadienyl ring), and 5·10 (tr; J = 5 c/s, α-methine protons).

A similar result was also obtained by LAH reduction of I, together with a small amount of HCl. The ratio of IIIa to IIIb was 1:8.

2,5-*Diferrocenylfuran* (IV)

(a) *With polyphosphoric acid.* To freshly prepared polyphosphoric acid (20·0 g) was added I (3·0 g) at 45–47° and stirred for 7 hr. The reaction mixture was poured into ice water (200 ml) and reduced with L-ascorbic acid. The reaction mixture was extracted with benzene the extracted was washed and dried. After evaporation of the solvent, the residue was dissolved in benzene, and chromatographed on alumina. The first elution with benzene gave IV (0·7 g; 24%) as red plates, m.p. 188–189°. (Found: C, 66·08; H, 4·49. $C_{24}H_{20}OFe_2$ requires: C, 66·11; H, 4·62%); IR spectrum (KBr): 1584, 1013, and 776 cm^{-1} (furan ring). NMR ($CDCl_3$) τ: 5·87 (s, cyclopentadienyl ring), 5·72 (tr, J = 2 c/s, β-protons of cyclopentadienyl ring), 5·35 (tr; J = 2 c/s, α-protons of cyclopentadienyl ring), 3·81 (s, furan ring). UV spectrum (EtOH); mμ (log ε): 226 (2·34), 281 (3·98), 323 (4·81), 449 (4·59).

Second elution with EtOAc gave the recovered starting material I (1·0 g), m.p. 188–189°.

(b) *With conc* H_2SO_4. To conc H_2SO_4 (3 ml) was added I (0·2 g) at room temp in stirring for 6 hr. After the reaction mixture was treated in a manner similar above (a), IV alone was obtained (0·03 g), m.p. and mixed m.p. 188–189°.

Catalytic hydrogenation of 2,5-*diferrocenylfuran* (IV)

(a) *With rhodium catalyst.* Rhodium–charcoal (0·7 g) was suspended in a soln of IV (0·2 g) in EtOH (70 ml) and reduction was carried out in H_2 at 20 atm/cm^2 at room temp for 2 hr. After being treated by the usual method, the residue was chromatographed on alumina and eluted: (1) hexane (first portion) gave unchanged starting furan IV (0·08 g); (2) hexane (second portion) gave *cis*-IIIb (0·12 g, 9% calculated from conversion of IV) as yellow needles, m.p. 126–127°, which was identical with authentic IIIb, m.p. 126–127°, by means of mixed m.p. and IR spectrum.

(b) *With Raney nickel catalyst.* Raney Ni (9 g) was suspended in a soln of IV (0·2 g) in EtOH (70 ml) and hydrogenated under the initial press of 130 atm/cm^2 at 110° for 10 hr. The reduction product were chromatographed on alumina and eluted. Elution with hexane gave VI as a red oil (0·02 g). (Found: C, 67·93; H, 6·62 $C_{12}H_{14}Fe$ requires: C, 67·32; H, 6·59%); NMR ($CDCl_3$) τ: 8·81 (tr; J = 7·5 c/s, methyl-protons), 7·62 (qu; J = 7·5 c/s, methylene protons), and 5·92, 5·88 (cyclopentadienyl ring).

The second elution with benzene gave V as yellow needles (0·1 g), m.p. 107–108°. (Found: C, 67·45; H, 6·10. $C_{24}H_{26}Fe_2$ requires: C, 67·66; H, 6·10%); NMR spectrum ($CDCl_3$) τ: 8·48 (2,3-methylene protons), 7·65 (1,4-methylene protons), 5·92, 5·89 (cyclopentadienyl ring).

(c) *With platinum catalyst.* PtO_2 (0·7 g) was suspended in a soln of IV (0·5 g) in EtOH (100 ml), HCl-saturated EtOH (5 drops), was added and hydrogenated at an initial press of 130 atm/cm^2 at 120° for 7 hr. The reduction product was chromatographed on alumina and elution with benzene gave V as yellow needles (0·2 g), m.p. 107–108°.

Clemmensen-Martin reduction of 1,2-*diferrocenoylethane* (I)

A soln of I (1·0 g) in toluene (30 ml) was refluxed for 24 hr with Zn-amalgam (2·0 g) in conc HCl (20 ml) and H_2O (5 ml). Then, conc HCl (2–3 ml) was added to the reaction mixture 4 times at 6 hr intervals. After removal of Zn-amalgam, the toluene layer was separated, washed with H_2O, dried and evaporated under a reduced press. The residue was chromatographed on alumina. The first elution with hexane afforded a red oil (0·15 g) which was identified with the previously obtained VI by IR and NMR spectra. The second elution with benzene afforded yellow needles (0·8 g) which was identical with authentic V by mixed m.p. and IR spectrum.

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