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ORGANOMETALLIC COMPOUNDS

XXXVIII *. CONDENSED-RING FERROCENOPHANES CONTAINING TWO BRIDGES

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Summary

A variety of ferrocenophanes containing two bridges and two six-membered condensed-rings have been synthesized. Three of them (XII, XV and XVI) are identical to the compounds which we previously reported to be tetrabridged ferrocenophanes. Thus, the structures of the products formed by cyclization of [4][3][4]ferrocenophanebutanoic acids (I and II) have been determined, and the description in the previous paper has been corrected. The NMR spectra of the dibridged ferrocenophanes and the synthetic intermediary products were examined. Through-space magnetic effects of substituents of the Cp ring on the protons and carbons of the second Cp ring are discussed.

Introduction

In a previous letter [2], we reported that the two compounds (**A** and **B**) formed by cyclization of [4][3][4]ferrocenophanebutanoic acids (I and II) with ClCOOEt/NEt_3/$AlCl_3$ were tetrabridged [4][3][4][4]ferrocenophanes (III and IV) **. In investigating the reaction further, one other cyclization compound (**C**) in addition to compound **A** was isolated from the reaction products of II. The reduction product (**D**) of **C** with $LiAlH_4$/$AlCl_3$ was the same as that of **A** (Scheme 1). Furthermore, [4][3][4][4]ferrocenophane synthesized via an alternative route [3] was not in agreement with compounds **D** and **E**, and chemical and detailed spectroscopic examinations suggested the presence of homoannularly cyclized rings.

An X-ray crystal structural study by Hillman et al. [4,5] proved that the

* For Part XXXVII, see ref. 1.

** The nomenclature of the ferrocenophanes and the numbering of the Cp rings in this paper are those used in the previous paper [1].

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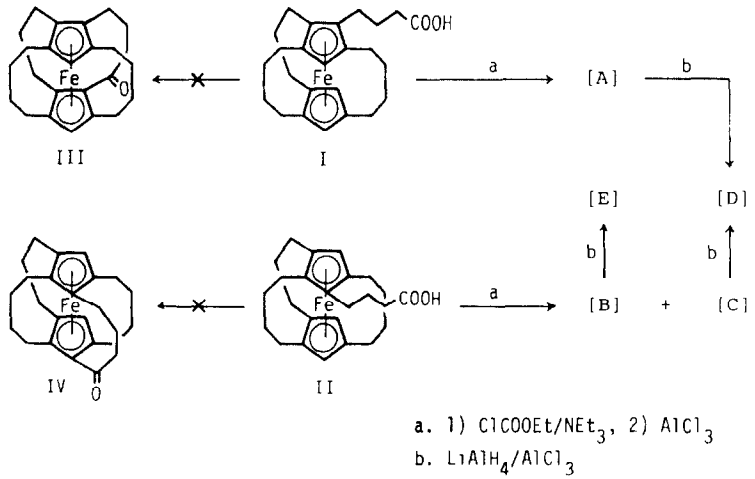
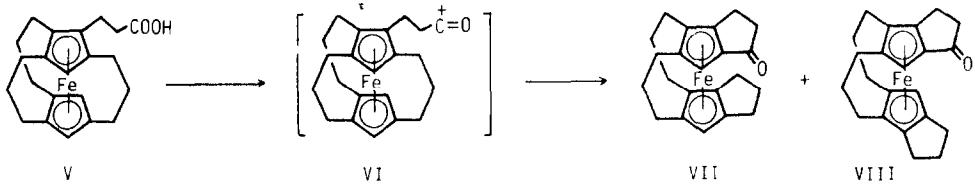


SCHEME 1. Unusual cyclization reactions of [4][3][4]ferrocenophanebutanoic acids (I and II).



SCHEME 2. Rearrangement of [3][3][3]ferrocenophanepropanoic acid [5].

cyclization products [6] obtained by treatment of [3][3][3]ferrocenophanepropanoic acid (V) with polyphosphoric acid (PPA) were not tetrabridged [3][3][3][3]ferrocenophanes but in fact condensed-ring ferrocenophanes (VII and VIII) (Scheme 2). They suggested that the unusual products were formed by attack of the intermediary acylium ion (VI) at the *ipso*-position of the existing bridge followed by rearrangement of the bridge to the homoannular cyclopentadienyl (Cp) ring. Accordingly, it was speculated that the unknown compounds (**A**, **B** and **C**) were homoannularly cyclized products formed via the same reaction mode as that of V. However, the structures of the products could not be confirmed by spectroscopy. We intended to determine their structures by synthesis via alternative routes. The reasons for adopting chemical means and not X-ray crystal analysis were as follows: (i) ferrocenophanes containing both bridges and condensed-rings had not been reported except as by-products in the preparation of bridged ferrocenophanes [4,5,7–12]; and (ii) these ferrocenophanes would be favorable for an NMR spectral examination of through-space magnetic effects of substituents of the Cp ring on the protons and carbons of the second Cp ring, because the two Cp rings are rigidly fixed to each other by the presence of bridges.

Results and discussion

Synthesis of condensed-ring ferrocenophanes

In selecting the target compounds, it was presumed that the reactions of butanoic acids I and II would proceed through Hillman's mechanism [4]. As shown in Scheme

3, the two intermediates IX and XIII generated from the acids would produce, respectively, three rearrangement products, X–XII and XIV–XVI, based on the positions of attack of the acylium ion and on the direction of the migration of the existing bridges. On the above assumption of the reaction mechanism, the unknown compounds (**A**, **B** and **C**) should be identical to three of the compounds X–XVI, or at least two of the deoxo derivatives of X–XVI should agree with the reduction products (**D** and **E**). Accordingly, we planned to synthesize all six compounds (X–XVI) and their deoxo derivatives.

Homoannular six-membered rings of the target compounds were built via acylation of [4]-oxo[3]ferrocenophanes with succinic anhydride followed by hydrogenolysis with PtO_2/AcOH, hydrolysis and cyclization with trifluoroacetic anhydride (TFAA), as summarized in Scheme 4. The corresponding deoxoferrocenophanes were easily oxidized to ferricenium ions under Friedel–Crafts conditions, even though the reaction was carried out under nitrogen or in a vacuum system. The use of oxoferrocenophanes as the substrate was more advantageous for either yields of the products or assignments of their structures than the use of deoxo derivatives.

The structural assignments of the isomeric products were confirmed by consideration of their yields and NMR spectral data. The first substitution reaction of XX

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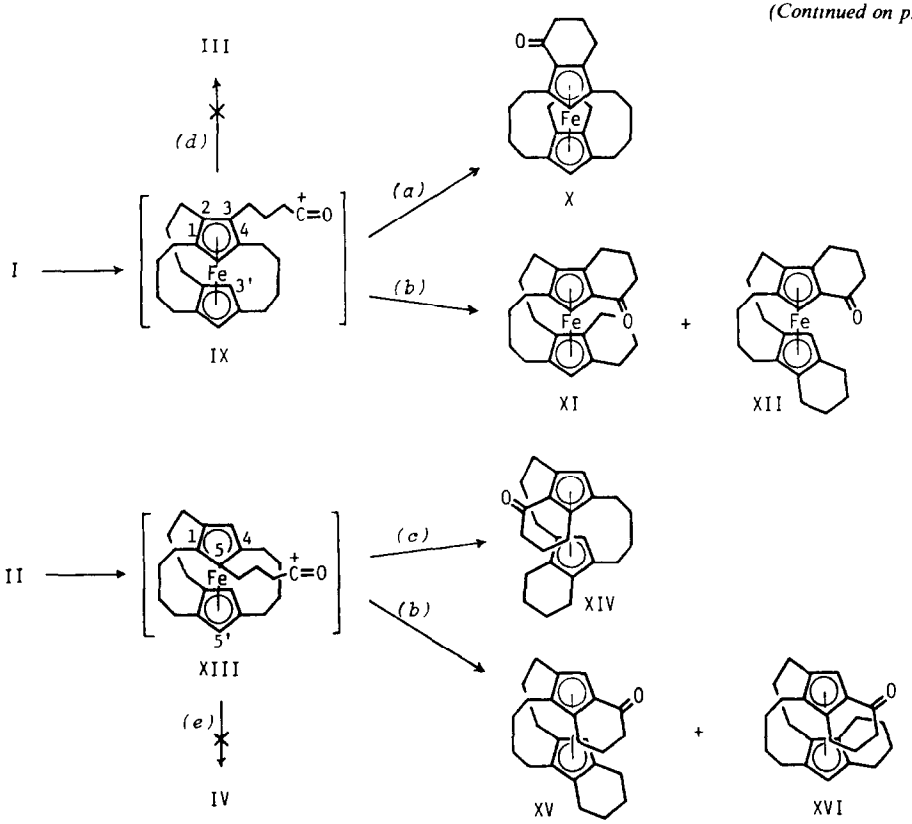
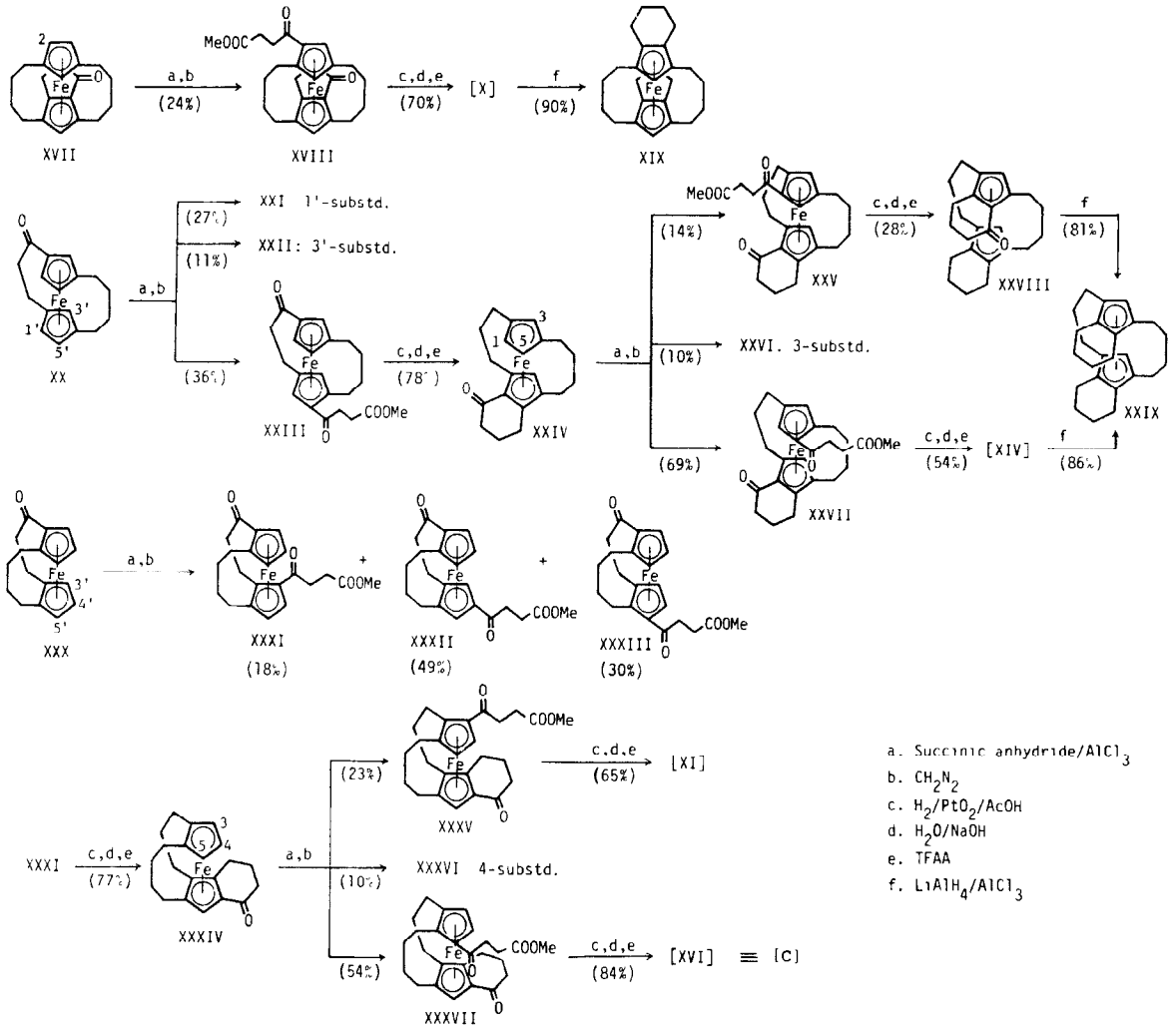
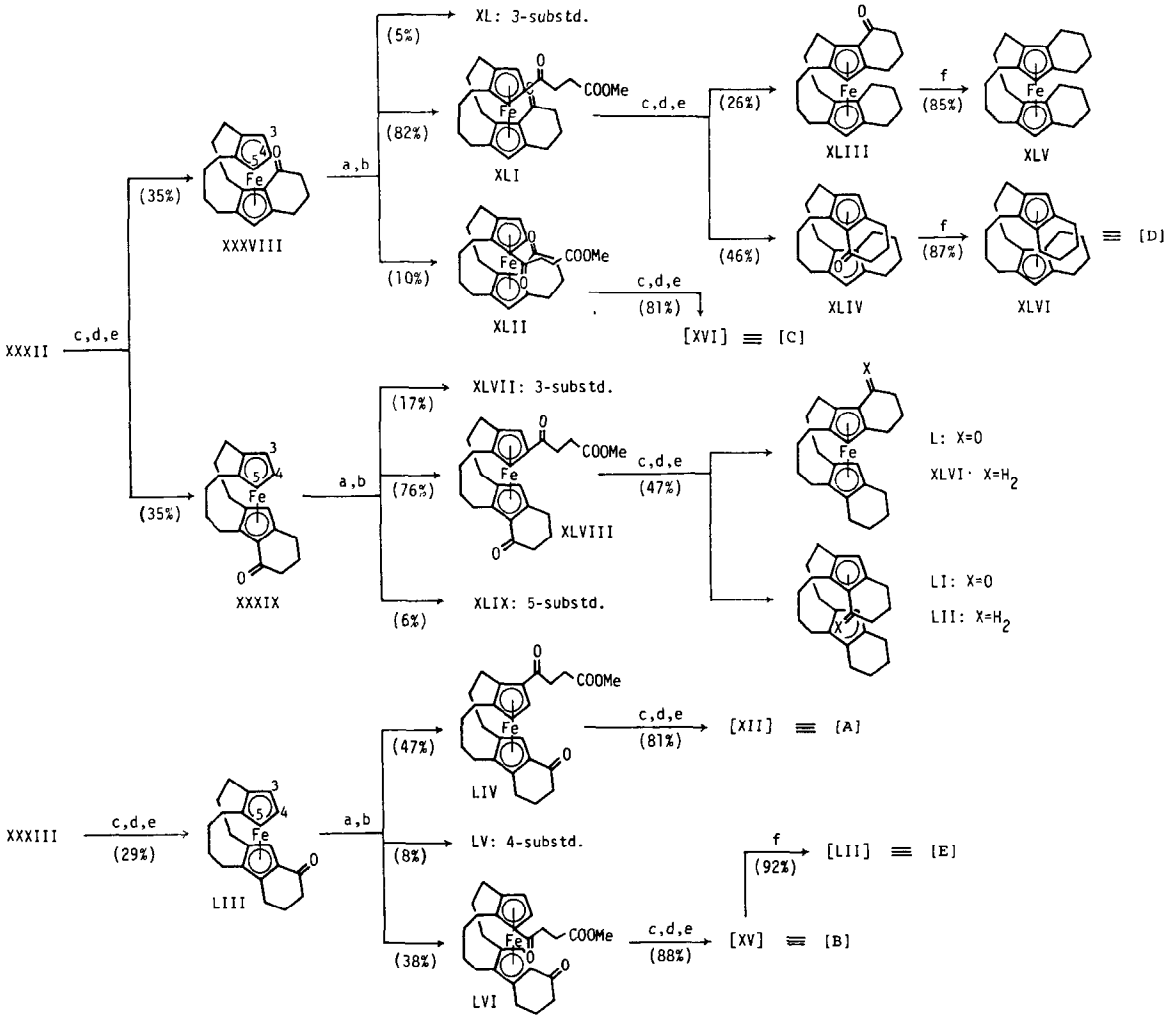


SCHEME 3. Possible pathways and products in the unusual cyclization of [4][3][4]ferrocenophanebutanoic acids (I and II). The symbols (a), (b), (c), (d) and (e) represent the attacks of the acylium ions in the intermediates (IX and XIII) at the 2-, 4-, 1-, 3′- and 5′-positions of the Cp rings, respectively.


XVII
a,b
(24%)
XVIII
c,d,e
(70%)
[X]
f
(90%)
XIX
XX
a,b
(27%)
XXI 1'-substd.
(11%)
XXII: 3'-substd.
(36%)
XXIII
c,d,e
(78%)
XXIV
a,b
(14%)
XXV
c,d,e
(28%)
XXVIII
f
(81%)
XXIX
(10%)
XXVI. 3-substd.
(69%)
XXVII
c,d,e
(54%)
[XIV]
f
(86%)
XXX
a,b
XXXI
(18%)
XXXII
(49%)
XXXIII
(30%)
XXXI
c,d,e
(77%)
XXXIV
a,b
(23%)
XXXV
c,d,e
(65%)
[XI]
(10%)
XXXVI 4-substd.
(54%)
XXXVII
c,d,e
(84%)
[XVI] ≡ [C]
a. Succinic anhydride/AlCl3
b. CH2N2
c. H2/PtO2/AcOH
d. H2O/NaOH
e. TFAA
f. LiAlH4/AlCl3



SCHEME 4. Synthesis of dibridged ferrocenophanes containing six-membered condensed-rings.

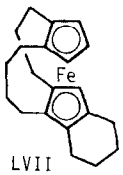
and XXX predominantly occurred at less sterically hindered positions of the Cp rings without a carbonyl group. In the second acylation of XXIV, XXXIV, XXXVIII, XXXIX and LIII, the positions attacked by the electrophilic agent were controlled not only by steric hindrance but also by the proximity of a carbonyl group on the condensed ring. Attack at the 4-position preferentially occurred in the acylation of 3′- and 5′-ketones (XXXVIII and XXXIX), while in the reaction of 4′-ketones (XXXIV and LIII) 4-acyl compounds (XXXVI and LV) were minor products.

As shown in Scheme 4, the unknown compounds **A**, **B**, **C**, **D** and **E** were identical to ferrocenophanes XII, XV, XVI, XLVI and LII, respectively. Therefore, it has been proved that the compounds produced by the cyclization of butanoic acids I and II were [4](1,1′)[3](2,2′)ferrocenophanes containing two six-membered condensed rings, and that they were formed via the same rearrangement of the existing bridge as that found in the trimethylene-bridging system by Hillman et al. [5]. The assignment of the cyclized compounds to tetrabridged ferrocenophanes (III and IV) in the previous letter [2] should be corrected. The formation of the unusual products has been discussed in the other paper [1].

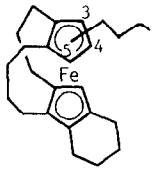
NMR spectra of condensed-ring ferrocenophanes

The ^{1}H NMR spectra of multibridged ferrocenophanes with trimethylene chains were reported by Rinehart et al. [7], and the spectra of some ferrocenophanes containing a five-membered condensed-ring were described. In this section, the chemical shift behavior of the Cp ring protons and carbons of the ferrocenophanes condensed with a six-membered ring are discussed with reference to the results of Rinehart et al.

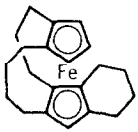
The nomenclature of the positions to the substituent is according to that of Rinehart. The *ipso*, α and β positions in the Cp ring to the substituent under discussion are symbolized by $\imath$, α and β, and the corresponding positions on the second Cp ring by i', α' and β'. For example, the 3-, 4-, 5-, 3′-, 4′- and 5′-carbons of XXXI are expressed as i'-, α'-, β'-, i-, α- and β-positions to the oxobutanoate side chain, respectively. Accordingly, the magnetic effect of the acyl group on the 3-, 4- and 5-protons can be called i'-, α'- and β'-effects, respectively. The signs (+) and (−) are used to indicate the magnetic shielding and deshielding effects, respectively. The chemical shifts and substituent effects are summarized in Tables 1–3, except for data remaining obscure in signal assignment and evaluation of the effect.



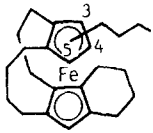
LVII



LVIII: 3-substd.
LIX: 4-substd.
LX: 5-substd.



LXI



LXII: 3-substd.
LXIII: 4-substd.
LXIV: 5-substd.

TABLE 1

CHEMICAL SHIFTS (δ, ppm) OF THE Cp RING PROTONS AND SUBSTITUENT EFFECTS ($\Delta\delta$) IN OXOBUTANOATE AND BUTANOATE DERIVATIVES OF FERROCENOPHANE IN $CDCl_3$

Compound	3′-H	$\Delta\delta$ [a]	Compound	5′-H	$\Delta\delta$ [a]
(a) Oxobutanoates					
LIII [b]	4.53	–	XXXIV [b]	4.64	–
LIV	4.38	+0.15(ι')	XXXVII	4.54	+0.10(ι')
LV	4.55	−0.02(α')	XXXVI	4.68	−0.04(α')
LVI	4.48	+0.05(β')	XXXV	4.58	+0.06(β')
XXXIX [b]	4.15	–	XXXVIII [b]	4.31	–
XLVII	4.12	+0.03(ι')	XLII	4.31	0.00(ι')
XLVIII	4.25	−0.10(α')	XLI	4.43	−0.12(α')
XLIX	4.06	+0.09(β')	XL	4.17	+0.14(β')
(b) Butanoates					
LVII [b]	3.72	–	LXI [b]	3.87	–
LVIII	3.25	+0.47(ι')	LXIV	3.66	+0.21(ι')
LIX	3.64	+0.08(α')	LXIII	3.80	+0.07(α')
LX	3.70	+0.02(β')	LXII	3.85	+0.02(β')

[a] Chemical shift difference from the corresponding proton shift of the standard compound. [b] Standard compound in each group.

(1) Acyl effect of methoxycarbonylpropanoyl group (Table 1(a)): In the series of 4′-ketones (XXXV–XXXVII, LIV–LVI), the ι'- and α'-effects of the acyl group on the protons of the second Cp ring are similar to Rinehart's results with acetylferrocenophanes. However, the ι'-effect in the 3′- and 5′-ketones (XL–XLII, XLVII–XLIX), which possess a carbonyl group on the homoannular ring at a position adjacent to the bridge, is very weak, while the (−)-α'-effect is fairly strong. A considerably strong (+)-β'-effect also appears in XL and XLIX in spite of the large distance between the protons and the acyl group. The unusual effects may be caused by a change in conformation. For example, the distances between the 5- and 5′-positions of XL and the 3- and 3′-positions of XLIX would be shorter than those of the standard compounds XXXVIII and XXXIX, respectively, due to mutual repulsion between the two carbonyl groups. It is known that such a proximity of Cp ring carbons in ferrocenophanes results in a deshielding shift of the corresponding proton signal [7].

(2) Alkyl effect of methoxycarbonylpropyl group (Table 1(b)): A clear-cut dependence of chemical shifts on distances between the Cp ring protons and the side-chain is shown; the diamagnetic shifts increase in the order of the β'-, α'- and ι'-positions. The stronger ι'-effect of LVIII than that of LXIV is obviously explained by the proximity of the corresponding proton to the alkyl group. The distances between the proton and the first carbon of the side-chain are 2.5 and 4.1 Å for LVIII and LXIV, respectively, from consideration of a Dreiding molecular model. The alkyl effect is not described in the paper of Rinehard et al. [7].

(3) Effect of the homoannular tetramethylene chain (Table 2(a)): The effect of the aliphatic chain on the protons of the second Cp ring is examined. The ι'-effect of the methylene chain is very strong (+0.40–+0.75 ppm). The larger shifts of XVI and XLIV than those of XII and L are interpreted by the circumstance that the 3-proton

TABLE 2

CHEMICAL SHIFTS (δ, ppm) OF THE Cp RING PROTONS AND EFFECTS OF THE HOMOANNULAR CHAIN ($\Delta\delta$) IN CONDENSED-RING FERROCENOPHANES IN $CDCl_3$

Compound	Proton	δ	$\Delta\delta$ [a]	Standard proton
(a) Effect of the cyclized tetramethylene chain				
i'-effect				
XII	5-H	4.24	+0.40	[b]
XVI	3-H	3.84	+0.69	[c]
XLIV	3-H	3.40	+0.75	[d]
L	5-H	3.86	+0.45	[e]
XLVI	3-H	2.99	+0.73	[f]
XLVI	5'-H	3.43	+0.44	[g]
α'-effect				
XI	5-H	4.70	−0.06	[b]
XV	3-H	4.54	−0.01	[c]
XLIII	5-H	4.26	+0.05	[e]
LI	3-H	4.07	+0.08	[d]
XLV	5-H	3.85	+0.02	[g]
LII	3-H	3.58	+0.14	[f]
(b) Effect of the carbonyl group of the homoannular chain				
i'-effect				
XLIV	5'-H	3.80	−0.37	[h]
L	3'-H	3.44	−0.45	[i]
α'-effect				
XI	5'-H	4.02	−0.17	[j]
XII	3'-H	3.41	−0.42	[i]
XV	3'-H	3.80	−0.22	[k]
XVI	5'-H	3.77	−0.34	[h]

[a] Chemical shift difference from the standard proton shift. [b] 5'-H(δ4.64) of XXXIV. [c] 3'-H(δ4.53) of LIII. [d] 3'-H(δ4.15) of XXXIX. [e] 5'-H(δ4.31) of XXXVIII. [f] 3'-H(δ3.72) of LVII. [g] 5'-H(δ3.87) of LXI. [h] 5'-H(δ3.43) of XLVI. [i] 3-H(δ2.99) of XLVI. [j] 5-H(δ3.85) of XLV. [k] 3-H(δ3.58) of LII.

is nearer to the first carbon of the homoannular chain than the 5-proton. The difference between the 3'- and 5'-proton shifts of XLVI also reflects very well the distance between the first carbon of the aliphatic chain and the Cp ring protons. The large *i'*-effect of the alkyl ring in comparison with that of the butanoate side chain mentioned in section (2) may be due to fixation of the alkyl chain by homoannular cyclizing. It is interesting that the shifts caused by the effect of the tetramethylene chain are larger than those of the trimethylene chain (+0.3 ppm) reported by Rinehart et al. [7].

The *α'*-effect of the aliphatic ring does not have a clear regularity and the shift values are small (−0.06– + 0.14 ppm).

(4) Effect of the carbonyl group in homoannular ketones (Table 2(b)): The effect is revealed by comparison of the Cp ring proton shifts of the ketones with those of the corresponding deoxo derivatives. Fairly large paramagnetic shifts were observed not only in the *i'*-protons (0.37–0.45 ppm) to the carbonyl group but also in the *α'*-protons (0.17–0.34 ppm). A consideration using a Dreiding molecular model leads

TABLE 3

CHEMICAL SHIFTS (δ, ppm) OF THE Cp RING AND CARBONYL CARBONS OF SELECTED FERROCENOPHANES IN C_6D_6

Compound	Cp ring carbons				Carbonyl carbons
	3-C	3'-C	5-C	5'-C	
XXXIV [a]	[b]	–	[b]	63.76	201.50
XI	–	–	64.52	65.40	200.79
XII	–	68.75	68.28	–	201.37
LIII [a]	[b]	63.70	[b]	–	201.73
XV	63.99	64.64	–	–	200.49
XVI	69.81	–	–	69.28	201.37
XXXVIII [a]	[b]	–	[b]	68.93	203.96
XLIII	–	–	68.10	65.58	202.37
XXXIX [a]	[b]	68.57	[b]	–	203.67
XLIV	74.45	–	–	69.87	204.01
LVII [a]	[b]	64.32	[b]	–	–
LXI [a]	[b]	–	[b]	64.91	–
LII	63.79	63.79	–	–	–
XLVI	70.51	–	–	69.39	–
XLV	–	–	64.23	64.23	–

[a] Standard compound for comparison of the corresponding Cp ring carbon signals in each group. [b] The chemical shift of the carbon is not described, because the assignment of the signal is obscure.

to a conformation in which both ι'- and α'-protons lie in the negative region of the carbonyl group anisotropy [13].

(5) ^{13}C NMR spectra (Table 3): The signals of the Cp ring carbons were assigned by selective irradiation of the corresponding protons (a selective decoupling technique). Only definitely assignable signals are shown in Table 3. The ι'-effect of the homoannular tetramethylene chain on the unsubstituted carbons of the second Cp rings is paramagnetic and fairly large (−4.52 (XII, 5-C), −6.11(XVI, 3-C), −5.88(XLIV, 3-C), −6.19(XLVI, 3-C) and −4.48(XLVI, 5'-C) ppm, in comparison with the corresponding carbon signals of the standard compounds XXXIV, LIII, XXXIX, LVII and LXI, respectively). The shift values depend on the distances between the Cp ring carbon and the first carbon of the aliphatic chain. The shift values caused by the α'-effect of the aliphatic chain are less than 1 ppm. The effect of the carbonyl group on the Cp ring carbons does not result in clearly regular shifts.

The chemical shifts of the carbonyl carbons are significantly influenced by the presence of the aliphatic chain on the second Cp ring, but the magnitudes of the shifts are small. The shift values of XI (+0.71 ppm) and XV (+1.24 ppm) in comparison with the standard compounds XXXIV and LIII, respectively, are apparently larger than those of XII (+0.13 ppm) and XVI (+0.36 ppm). This fact is explained by steric hindrance between the two homoannular rings of compounds XI and XV, because the tetramethylene chains are cyclized at the symmetric positions on the two Cp rings. The homoannular rings of XII and XVI are at the asymmetric positions, and their steric interaction may be small.

Experimental

Synthesis was carried out according to the general procedures mentioned below. The physical properties and spectral data of the new ferrocenophanes are sum-

TABLE 4

PHYSICAL PROPERTIES AND SPECTRAL DATA OF FERROCENOPHANES

Compound	Properties, m.p. (°C)	IR [a] (cm^{-1})	^1H NMR (δ) in $CDCl_3$ [b]
X	red needles 166–168	1650	3.80(1H,s,5′-H), 4.35(1H,s,5-H)
XI	orange flakes 230 (dec.)	1655	4.02(1H,s,5′-H), 4.70(1H,s,5-H)
XIV	red crystals 190–192	1655	3.69(1H,s,3′-H), 4 17(1H,s,3-H)
XIX	yellow plates 127–128	–	3.85 and 3.87(each 1H,s,5,5′-H)
XXI	yellow crystals 117–119	1730 1680 1660	3.72(3H,s,–COOMe), 4.36(1H,dd,1.3,2 4, 5-H), 4 76(1H,dd,1.3,2.4,1-H), 4.85(1H,t,1.3,3-H), 4 93(1H,d,1.5, 3′-H), 4 97(1H,d,1.5,5′-H)
XXII	red oil	1735 1685 1660	3.72(3H,s,–COOMe), 3.98(1H,dd,1 5, 2.3,5-H), 4.31(1H,dd,1.5,2.3,1-H), 4.43 and 4.68(each 1H,AB,2 5,1′,5′-H), 4.75(1H,t,1.5,3-H)
XXIII	yellow needles 163–165	1730 1685 1665	3.73(3H,s,–COOMe), 4.39 and 4.57(2H,1H, ABX,1,3,5-H), 4.76(1H,d,1.5,3′-H), 4.81(1H,d,1.5,1′-H)
XXIV	orange needles 166–168	1660	3.55(1H,dd,1.3,2.1,5-H), 3.89(1H,t, 1.3,3-H), 4.11(1H,dd,1.5,2.1,1-H), 4.25(1H,s,3′-H)
XXV	red crystals 133–135	1730 1660 1645	3.68(3H,s,–COOMe), 4.17 and 4.22(each 1H, AB,1.5,3,5-H), 4.21(1H,s,3′-H)
XXVI	red oil	1740 1665	3.68(3H,s,–COOMe), 4.21 and 4.23(each 1H, AB,2.5,1,5-H), 4.32(1H,s,3′-H)
XXVII	orange crystals 161–163	1740 1655	3.68(3H,s,–COOMe), 4.15(1H,s,3′-H), 4.22(1H,d,1.5,3-H), 4.56(1H,d,1 5,1-H)
XXVIII	red crystals 125–127	1655	3.67(1H,s,3′-H), 4.23(1H,s,3-H)
XXIX	yellow crystals 134 (dec.)	–	3.74(2H,s,3,3′-H)
XXXI	orange-red needles 136–137	1730 1655	3.75(3H,s,–COOMe), 4.11(1H,dd,1 4,2.6, 5-H), 4.27(1H,d,2.7,5′-H), 4.47(1H,t, 2.6,4-H), 4.57(1H,d,2.7,4′-H), 4 73 (1H,dd,1.4,2.6,3-H)
XXXII	orange-red needles 130–131	1740 1660	3.71(3H,s,–COOMe), 4.35 and 5 02(2H,1H, ABX,3,4,5-H), 4.57 and 5.24(each 1H,AX, 1 4,3′,5′-H)
XXXIII	orange-red needles 143–144	1725 1660	3.69(3H,s,–COOMe), 4.25(1H,dd,1.4,2.5, 5-H), 4.37(1H,t,2.5,4-H), 4.73(2H,m, 3,3′-H), 4.81(1H,d,2.6,4′-H)
XXXIV	orange needles 171–173	1650	3.60 and 4.13(1H,2H,ABX,3,4,5-H), 4.64 (1H,s,5′-H)
XXXVII	orange needles 118–119	1720 1660	3.69(3H,s,–COOMe), 3.81(1H,d,2 8,3-H), 4.54(1H,s,5′-H),4.60(1H,d,2.8,4-H)
XXXVIII	red-brown prisms 123–124	1660	3.67(1H,dd,1.4,2.4,3-H), 3.92(1H,dd, 1.4,2.4,5-H), 4.07(1H,t,2.4,4-H), 4.31(1H,s,5′-H)
XXXIX	red-brown prisms 96–97	1655	3.85 and 4.05(2H,1H,ABX,3,4,5-H), 4.15 (1H,s,3′-H)

TABLE 4 (continued)

Compound	Properties, m.p. (°C)	IR [a] (cm^{-1})	^1H NMR (δ) in $CDCl_3$ [b]
XLI	red needles	1740	3.69(3H,s,–COOMe), 4.34(1H,d,1.4,3-H),
	147–149	1655	4.43(1H,s,5′-H),4.50(1H,d,1.4,5-H)
XLII	orange oil	1740	3.72(3H,s,–COOMe), 3.91(1H,d,2.8,3-H),
		1660	4.31(1H,s,5′-H), 4.55(1H,d,2.8,4-H)
XLIII	red prisms	1655	3.74(1H,s,5′-H), 4.26(1H,s,5-H)
	162–164		
XLIV	red prisms	1660	3.40(1H,s,5′-H), 3.80(1H,s,3-H)
	148–150		
XLV	yellow crystals	–	3.85(2H,s,5,5′-H)
	179–181		
XLVII	orange-red oil	1735	3.72(3H,s,–COOMe), 4.12(1H,s,3′-H),
		1660	4.26(1H,d,2.6,5-H), 4.57(1H,d,2.6,4-H)
XLVIII	orange needles	1750	3.69(3H,s,–COOMe), 4.25(1H,s,3′-H),
	151–152	1730	4.45(1H,d,1.4,5-H), 4.59(1H,d,1.4,3-H)
		1660	
XLIX	orange-red needles	1735	3.68(3H,s,–COOMe), 4.06(1H,s,3′-H),
	141–143	1665	4.12(1H,d,2.6,3-H), 4.45(1H,d,2.6,4-H)
LIII	orange needles	1660	3.98(3H,m,3,4,5-H), 4.53(1H,s,3′-H)
	159–160		
LIV	yellow flakes	1715	3.68(3H,s,–COOMe), 4.19(1H,d,2.6,5-H),
	128–130	1660	4.38(1H,s,3′-H), 4.62(1H,d,2.6,4-H)
LV	orange-red flakes	1740	3.66(3H,s,–COOMe), 4.48 and 4.56(each 1H,
	178–179	1660	AX,1.4,3,5-H), 4.55(1H,s,3′-H)
		1645	
LVI	orange needles	1740	3.69(3H,s,–COOMe), 4.34 and 4.40(each 1H,
	146–148	1725	AB,2.9,3,4-H), 4.48(1H,s,3′-H)
		1655	

[a] The IR spectra were measured in KBr disk and neat liquid on NaCl plates, respectively, for crystalline and oily compounds. [b] Relative intensities, multiplicities, coupling constants (Hz), and assignments are in parentheses. AB, AX and ABX represent patterns of AB, AX and ABX systems, respectively.

marized in Table 4. Molecular weights of all the compounds were determined by mass spectrometry. Combustion elemental analyses (for solids) or high-resolution mass spectra (for oily or unstable compounds) gave sufficient results. The instruments used for spectral measurements have been described in the other paper [12]. The data of compounds XII, XV, XVI, XLVI and LII which agreed with the unknown compounds A–E have been reported in the previous paper [1]. Oxobutanoate XVIII has already been described [1]. Ferrocenophanes XXXV, XXXVI, XL, L and LI could not be isolated even by means of high-performance liquid chromatography, but their structures and signal assignments of the ^1H NMR spectra were confirmed by the spectra of the mixtures. Their ^1H NMR spectral data are not described in Table 4 but in Tables 1 and 2.

General procedures

Friedel–Crafts acylation. [4][3]Ferrocenophanes used as starting materials were prepared by methods reported by us previously [9,10]. To a suspension of succinic anhydride (2 mol equiv. to substrate) and aluminium chloride (4 mol equiv. to substrate) in dry dichloromethane was added dropwise a solution of oxofer-

rocenophane in dry dichloromethane at 0°C under nitrogen. The reaction mixture was stirred at 0°C for 1 h, and then poured into ice-water containing ascorbic acid. The dichloromethane extracts were washed with saturated aqueous NaCl and dried over Na_2SO_4, and the solvent was removed with a rotary evaporator. The residue was dissolved in benzene, and a solution of diazomethane in ether was added to the above solution of the product. The residue which resulted from evaporation of the solution was column-chromatographed over silica gel with hexane/benzene or hexane/ethyl acetate as eluant to separate it into several isomers of acyl-oxoferrocenophane. The isolated products were recrystallized from hexane/ethyl acetate.

Catalytic hydrogenolysis of oxobutanoate derivatives. PtO_2 (10% (w/w) of substrate) was added to a solution of the oxobutanoate derivative in acetic acid, and the mixture was shaken under hydrogen at a pressure of ca. 4.8 kg/cm^2 for 24 h. Benzene was added to the reaction mixture followed by neutralization with saturated aq. Na_2CO_3 containing ascorbic acid. The benzene layer was separated, washed with saturated aqueous NaCl and dried over Na_2SO_4. The residual crude of the reduction product obtained by evaporation was purified by column-chromatography over silica gel. The butanoates were used for the following hydrolysis without further purification, because almost all of them were unstable in solvent. Their structures were confirmed by high-resolution mass spectrometry and ^1H NMR spectroscopy.

Hydrolysis of butanoates and cyclization of the resulting butanoic acids. A solution of methyl butanoate in ethanol and 20% aqueous NaOH was stirred at 80°C for 15 min. After neutralization with 6 *N* HCl, the product was extracted with benzene. The extracts were washed with saturated aqueous NaCl and dried over Na_2SO_4. The residual crude of butanoic acid obtained by evaporation of the solution was used for the following cyclization without further purification.

A solution of butanoic acid in dry dichloromethane was added dropwise to a solution of trifluoroacetic anhydride (150% (w/w) of substrate) in dry dichloromethane at 0°C under nitrogen. The reaction mixture was stirred below 10°C for 5 h, and poured into ice-water. The hydrolysate was neutralized with saturated aqueous Na_2CO_3 containing ascorbic acid and extracted with dichloromethane. The extracts were washed with saturated aqueous NaCl and dried over Na_2SO_4. The solvent was removed with an evaporator and the residue was column-chromatographed over silica gel with hexane/ethyl acetate (5/1). Separation of isomers XXXVIII and XXXIX was carried out by a Merck pre-packed column of LiChroprep Si-60 connected to a Hitachi 635-A HPLC, because separation with a usual open column could not be achieved.

Reduction of oxoferrocenophanes with $LiAlH_4/AlCl_3$. A solution of ketone in dry ether was added dropwise to a suspension of $LiAlH_4$ and $AlCl_3$ in ether at 0°C. The reaction mixture was stirred at room temperature for 2 h and then hydrolysed with moist ether. After water was added, the ether extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4 and evaporated. The resulting crude was column-chromatographed over alumina, and the reduction product obtained was recrystallized from hexane.

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