Journal of Organometallic Chemistry, 266 (1984) 147–157
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOMETALLIC COMPOUNDS

XXXVII *. BRIDGE REARRANGEMENTS OF MULTIBRIDGED FERROCENOPHANES IN THE PRESENCE OF ALUMINUM CHLORIDE

MASAO HISATOME *, YOSHIKI KAWAJIRI, JUN WATANABE, MASAHIRO YOSHIOKA and KOJI YAMAKAWA

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-Funagawara, Shinjuku-ku, Tokyo 162 (Japan)

(Received June 2nd, 1983)

Summary

Two bridge-rearrangement reactions with $AlCl_3$ have been found in the cyclization of [4](1,1′)[3](2,2′)[4](4,4′)ferrocenophanebutanoic acids (XIb and XIIb) and in the Friedel–Crafts acylation of [4](1,1′)-α-oxo[3](2,2′)[4](4,4′)ferrocenophane (I). The cyclization of XIb and XIIb with $ClCO_2Et/NEt_3/AlCl_3$ gives no tetrabridged ferrocenophane but three dibridged ferrocenophanes (XVII, XVIII and XIX) each containing two six-membered condensed-rings which are formed via homoannular cyclization of the side chains followed by rearrangement of the existing tetramethylene bridges. Various multibridged ferrocenophanes were treated with $AlCl_3$ to account for the reaction mode in the rearrangement of I, and evidence for selective acyl migration of the oxotrimethylene bridge to the other cyclopentadienyl ring has been obtained.

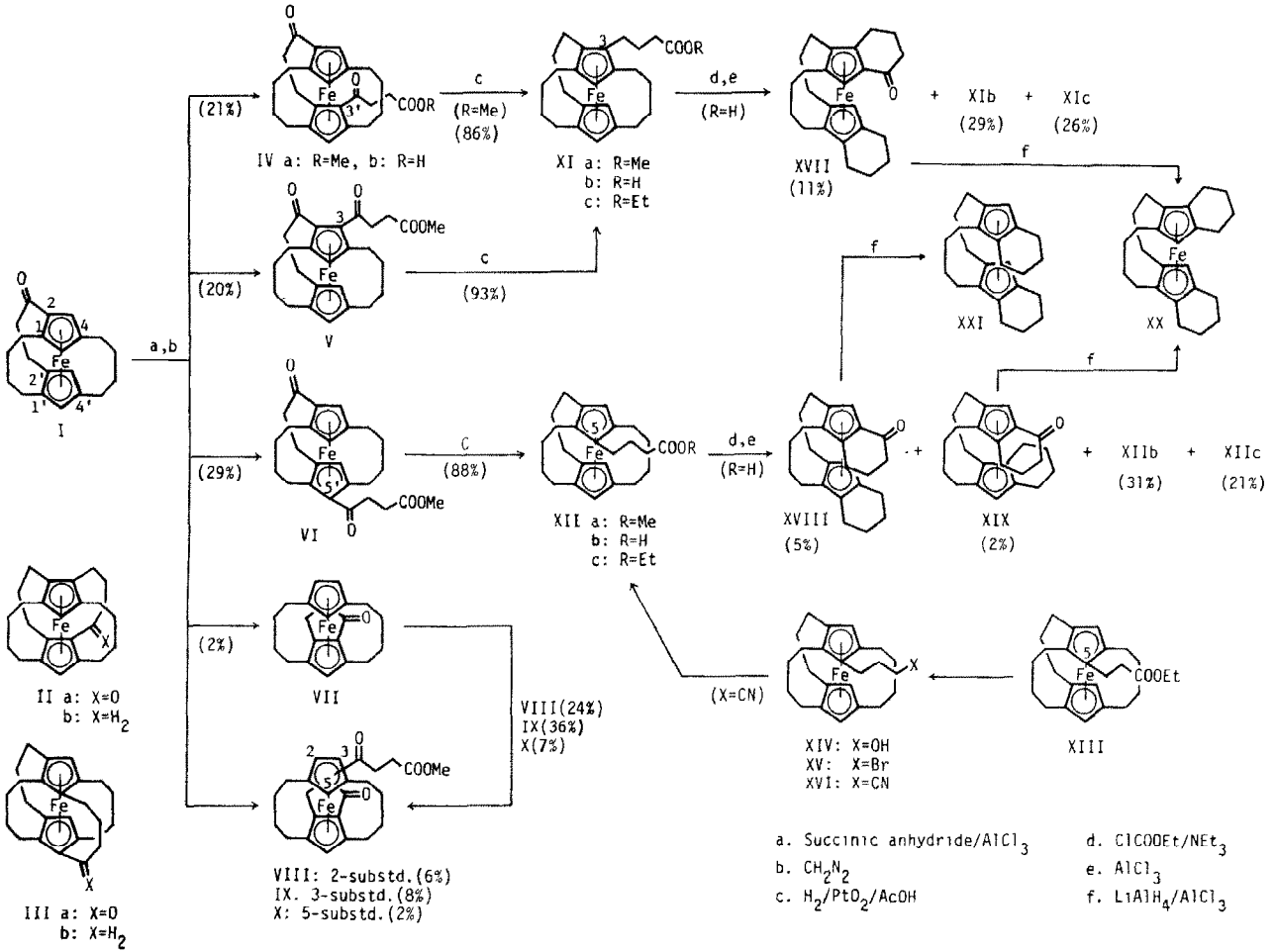
Introduction

In our series of the study of multibridged ferrocenophanes with tetramethylene chains [1–8], we previously reported the synthesis of tetrabridged ferrocenophanes (II and III) by cyclization of [4][3][4]ferrocenophanebutanoic acids (XIb and XIIb) with $ClCO_2Et/NEt_3/AlCl_3$ in a letter [9]. However, further synthetic examination via alternative routes [10] has shown that their structures should be revised to contain two homoannularly condensed rings (XX and XXI). It was revealed that both homoannular cyclization of the side-chains and rearrangement of the existing tetramethylene bridges occurred in the intramolecular electrophilic acylation of XIb

* For part XXXVI, see ref. 1.

0022-328X/84/$03.00

SCHEME 1. Synthesis and bridge rearrangement of [4][3][4]ferrocenophanebutanoic acid derivatives.



and XIIb with $AlCl_3$. Although a similar reaction has been found in the cyclization of [3][3][3]ferrocenophanepropanoic acid by Hillman and coworkers [11,12], the present result is of interest as an example of the migration of the unstrained tetramethylene bridge.

In addition, a rearrangement of the oxomethylene bridge to form a homoannular ring has also been found in the preparation of XIb and XIIb. Dibridged [4][4]ferrocenophane (VII) was formed in the Friedel–Crafts reaction of tribridged [4][3][4]ferrocenophane (I) with succinic anhydride/$AlCl_3$. This reaction mode has been elucidated by investigation of the reactions of various ferrocenophanes containing an oxomethylene bridge with $AlCl_3$.

We now wish to report those rearrangement reactions of multibridged ferrocenophanes * in the presence of $AlCl_3$.

Results and discussion

Bridge rearrangement in the cyclization of [4][3][4]ferrocenophanebutanoic acids

On cyclization of ferrocenebutanoic acid with condensation reagents, a homoannular six-membered ring is formed but no heteroannularly bridged compound, while the reaction of ferrocenepropanoic acid under the same conditions selectively affords a bridged compound [14]. Accordingly, formation of the tetramethylene bridge cannot be achieved by one-step reaction, and must proceed via bridge-enlargement of α-oxo[3]ferrocenophanes, prepared by bridging of the corresponding propanoic acid derivatives [2–4,6,15]. However, the bridge formation is expected for butanoic acid derivatives in which both sides adjacent to the carboxyalkyl side-chain on the cyclopentadienyl (Cp) ring are occupied by two bridges. We attempted to synthesize tetrabridged [4][3][4][4]ferrocenophanes (II and III) by one-step formation of the tetramethylene bridge from XIb and XIIb.

[4]-α-Oxo[3][4]ferrocenophane (I) was used as the starting material, because the reaction of its deoxoferrocenophane gives only small amounts of acylation products [10]. The Friedel–Crafts reaction of I followed by treatment with diazomethane yielded three normal acylation products (IVa, V and VI), a homoannularly cyclized compound (VII), and three dibridged acylferrocenophanes (VIII–X) (Scheme 1).

Ferrocenophane VII was identical to [4](1,1′)[3](2,3)[4](4,4′)ferrocenophane already described [3], and acylation of VII gave the three compounds VIII, IX and X in a similar ratio to that in the above acylation. Ketone I was treated with $AlCl_3$ in dichloromethane to give a dibridged ferrocenophane (VII) in a good yield. These results show that the oxotrimethylene bridge of I migrates under Friedel–Crafts conditions with $AlCl_3$. A further detailed examination using various α-oxoferrocenophanes to account for the reaction mode will be described in the following section.

Catalytic hydrogenolysis of both acyl compounds IVa and V in HOAc gave the same product (XIa). On the other hand, the compound XIIa obtained by hydrogenolysis of VI was identical to methyl 5-[4][3][4]ferrocenophanebutanoate, which

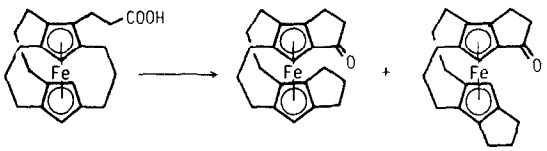
* The nomenclature of the ferrocenophanes in the present paper is a modification of that proposed by Vögtle and Neumann [13]. The modified numbering of the cyclopentadienyl rings, as shown in the schemes, is adopted for convenience for comparison of the substituted positions of the products with the corresponding starting materials.

was derived by elongation of the side chain of 5-[4][3][4]ferrocenophanepropanoate (XIII) via four steps. The structure of XIII has already been determined by X-ray crystal analysis of its derivative, [4][3][4][3]ferrocenophane [16]. Thus the position of the side-chain of VI and of XII was determined, and the structures of the isomeric butanoic acid derivatives IV, V and XI were also confirmed, as illustrated in Scheme 1.

Treatment of XIb or XIIb with trifluoroacetic anhydride, a typical reagent for bridging, led only to the recovery of the starting materials. Reaction of the acids with ethyl chlorocarbonate and triethylamine followed by the addition of $AlCl_3$ produced a number of products. Chromatography of the crude mixtures resulted in the isolation of three compounds, XVII, XVIII and XIX, together with the starting materials and ethyl esters XIc and XIIc. The formation of the ethyl esters is possibly due to esterification of the acids XIb and XIIb with ethyl chlorocarbonate. Reduction of both ketones XVII and XIX with $LiAlH_4/AlCl_3$ gave the same product (XX), indicating that XVII and XIX are regioisomeric about the carbonyl group. The NMR spectra and TLC behavior of the ketones XVII, XVIII and XIX and the reduction products XX and XXI suggested that they were homoannularly cyclized compounds rather than the expected bridged ferrocenophanes. Consequently, synthesis of these compounds via alternative routes was attempted, and their dibridged structures containing two six-membered condensed rings were chemically determined, as described in the subsequent paper [10].

Hillman and coworkers [11,12] reported that when [3][3][3]ferrocenophanepropanoic acid (XXII) was treated with polyphosphoric acid only XXIII and XXIV were obtained (Scheme 2), and suggested that the products were formed by the

SCHEME 2. Bridge rearrangement of [3][3][3]ferrocenophanepropanoic acid [11,12].



XXII XXIII XXIV

attack of an acylium ion at the *ipso*-position of the existing bridge, and by subsequent rearrangement of the bridge. Cyclization of XXII with $ClCO_2Et/NEt_3/AlCl_3$ also gave XXIV but no tetrabridged ferrocenophane [17]. The trimethylene chain is too short to bridge the two Cp rings of ferrocene (3.32 Å [18]) without strain. Accordingly, the bridging of strained [3][3][3]ferrocenophane with this chain would introduce additional strain, but the formation of rearrangement products XXIII and XXIV would release a considerable amount of strain, as described by Hillman et al. [11]. On the other hand, a tetramethylene bridge would hardly cause any strain to the molecule because the chain is long enough to bridge the two Cp rings. An attempt to synthesize unstrained [4][4][4]ferrocenophane by cyclization of 2-[4](1,1′)[4](3,3′)ferrocenophanebutanoic acid was also unsuccessful, and only produced some rearrangement products [17]. These results show that the formation of the tetramethylene bridge cannot be achieved by one-step cyclization of the butanoic acid side-chain, even though both sides of the chain on the Cp ring are blocked by

bridges. It is suggested that the butanoic acid side-chain cannot essentially bridge the ferrocene nucleus in spite of favorable bridging without strain.

Bridge rearrangement of oxomethylene chains in multibridged α-oxoferrocenophanes

Ferrocenophane VII containing a five-membered condensed-ring is formed in the Friedel–Crafts reaction of [4]-α-oxo[3][4]ferrocenophane (I), as mentioned previously. The selective rearrangement of the oxotrimethylene bridge to form a homoannular ring would be different in mechanism from the unusual cyclization of butanoic acids XIb and XIIb described in the previous section. Slocum et al. [19] reported the racemization of an optically active α-oxo[4](1,2)ferrocenophane by treatment with $AlCl_3$ in refluxing nitromethane, and suggested the occurrence of a substituted Cp ring-iron bond fission. A similar ligand exchange of alkylferrocene with $AlCl_3$ was reported by Bublitz [20]. However, their mechanism cannot apply to the rearrangement of tribridged ferrocenophane I, because the reaction proceeds with preservation of the bridged structure. Therefore, bridge rearrangement with $AlCl_3$ was investigated in detail by using various types of α-oxoferrocenophanes.

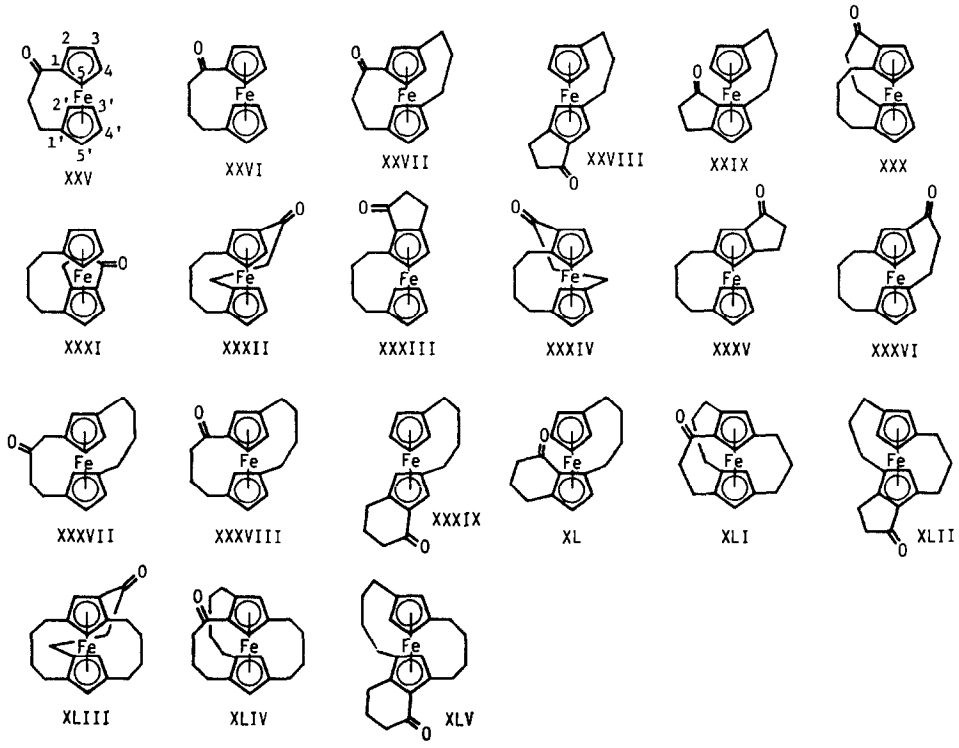
The reactions were carried out by stirring a suspension of the corresponding ferrocenophane and $AlCl_3$ (10 mol equiv. to the substrates) in dichloromethane at room temperature. The results are summarized in Table 1. The [4]-α-oxo[3]ferrocenophanes XXX and XXXII were employed to determine whether the cleavage

TABLE 1

BRIDGE REARRANGEMENT OF α-OXOFERROCENOPHANES WITH $AlCl_3$ IN DICHLOROMETHANE

Substrate	Recovered Starting material (%)	Products		
		Compound	Yield (%)	Total yield (%)
Monobridged ferrocenophanes				
XXV	57	–	–	–
XXVI [a]	66	–	–	–
Dibridged ferrocenophanes				
XXVII	51	XXVIII	13	16
		XXIX	2.5	
XXX	46	XXXI	34	42
		XXXII	8.2	
XXXII	50	XXXI	44	48
		XXX	3.8	
XXXVI	93	–	–	–
XXXVII	quant.	–	–	–
XXXVIII	80	XXXIX	8.1	17
		XL	9.0	
Tribridged ferrocenophanes				
XLI [a]	–	XLII	88	88
I	24	VII	74	74
XLIII	–	VII	74	74
XLIV [a]	5.8	XLV	84	84

[a] Small amounts of unknown products are given.



occurred in the Cp ring–acyl or the Cp ring–alkyl bond of the oxomethylene bridge. Treatment of XXX with $AlCl_3$ gave only XXXI and XXXII together with the recovered starting material, but neither XXXIII nor XXXIV. The reaction of slanting-bridged ferrocenophane XXXII also produced only XXX and XXXI but no XXXV and XXXVI. Therefore it is evident that the Cp ring–acyl bond is selectively cleaved, and that the resulting acylium ion or analogous active site migrates to the other positions. Selective Cp ring–acyl bond cleavage is supported by the facts that the oxotetramethylene bridge of α-oxoferrocenophane XXXVIII could be rearranged, but the reaction of β-oxoferrocenophane XXXVII gave no rearrangement product. There is no report on the acyl migration of ferrocenophanes and other phanes with Lewis acids, although alkyl migrations of ferrocene derivatives [20,21] and skeletal rearrangements of phanes [22,23] are known.

Friedel–Crafts acylation is usually considered to be an irreversible reaction [24] and free of rearrangement [25], in contrast to Friedel–Crafts alkylation. Recently, some examples of remarkable reversibility in Friedel–Crafts acylation and of acetyl exchange under Friedel–Crafts conditions were reported [26,27]. The present rearrangement is also considered to be a migration involving a "retro Friedel–Crafts process". An acylium ion analogous to the intermediate in the Friedel–Crafts reaction would be formed by attack of an electrophile * followed by Cp ring–acyl

* The species is presumably trace amounts of proton which were generated by decomposition of $AlCl_3$ with moisture.

bond fission, as shown in the acyl migration of fluorofluorenone [26b]. Subsequent electrophilic substitution of the acylium ion at the Cp ring would be governed by the thermodynamic stability of the product. The presence of aliphatic methylene bridges may be a dominant factor for Cp ring–acyl bond cleavage in α-oxo[4]ferrocenophanes, because an increase in the number of bridges results in an increase in the yields of the rearrangement products.

The yields of the products in α-oxo[3]ferrocenophanes are almost similar to those of the corresponding α-oxo[4]ferrocenophanes, except for XXXVI. This result seems to show that the rearrangement is not accelerated by strain in the substrates. However, the tribridged ferrocenophanes I, XLI and XLIII were quantitatively converted to VII, XLII and VII, respectively, in small-scale reactions *, while the yield of XLV in the reaction of XLIV was 84% at best. Furthermore, it is neccessary to take into account the possibility that the cleaved Cp ring–acyl bonds in the compounds bridged with the α-oxotrimethylene chain are recombined to bridge. In fact, the bridged products were preferentially formed in the cyclization of the corresponding ferrocenophanepropanoic acids [3,28]. The almost quantitative recovery of the starting material in the reaction of XXXVI supports the occurrence of bridge reformation, in consideration of the selective bridging in the cyclization of 3-[4]ferrocenophanepropanoic acid to give XXXVI. Therefore it seems reasonable to assume that the effect of strain in the substrate on cleavage of the Cp ring–acyl bond, besides the alkyl effect of the bridge, is significant in the rearrangement of multibridged ferrocenophanes with the α-oxotrimethylene chain.

Experimental

The physical properties and spectral data of the new compounds are summarized in Table 2. All the solids were recrystallized from hexane/ethyl acetate. Melting points are uncorrected. The molecular weights of all the compounds were determined by mass spectrometry. Combustion elemental analyses (for solids) or high-resolution mass spectra (for oily and unstable compounds) gave sufficient results. All spectra were obtained from the same spectrometers as those used in the previous paper [16].

Friedel–Crafts acylation of [4][3][4]ferrocenophanes (I and II)

Succinic anhydride (117 mg, 1.17 mmol) and $AlCl_3$ (312 mg, 2.34 mmol) were added to dry dichloromethane under nitrogen, and the mixture was stirred at room temperature and then cooled to 0°C. To the suspension was added dropwise a solution of [4]-α-oxo[3][4]ferrocenophane (I) (204 mg, 0.586 mmol) in dry dichloromethane. The mixture was stirred at room temperature for 15 h, and then poured into ice-water containing ascorbic acid. The dichloromethane extracts were washed with saturated aq. NaCl, dried over $CaCl_2$ and evaporated. A solution of diazomethane in ether was added to a solution of the above reaction product in benzene, and the solvents were evaporated. The residue was column-chromatographed over silica gel with hexane/benzene/acetone (30/10/1) to yield seven compounds. Separation of IVa and V was carried out by TLC over silica gel on a preparative scale with benzene.

* These results are not described in Table 1 because of the different reaction conditions (substrates: ca. 0.03 mmol).

TABLE 2. PHYSICAL PROPERTIES AND SPECTRAL DATA OF FERROCENOPHANES

Compound	Property, m.p. (°C)	IR [a] (cm^{-1})	NMR (δ) in $CDCl_3$ [b]
IVa	orange oil	1733, 1670, 1663	3.72(3H,s,-COOMe), 4.10(1H,s,5'-H), 4.15(1H,d,1.6,5-H), 4.88(1H,d,1.6,3-H)
IVb	orange crystals, 170 (dec.)	1710, 1670, 1663	4.12(1H,s,5'-H), 4.16(1H,d,1.5,5-H), 4.89(1H,d,1.5,3-H)
V	orange crystals, 129–131	1730,1678, 1668	3.71(3H,s,-COOMe), 3.87(1H,d,1.6,5'-H), 4.37(1H,s,5-H), 4.66(1H,d,1.6,3'-H)
VI	orange plates, 127–128	1730, 1675, 1660	3.70(3H,s,-COOMe), 4.19(1H,d,1 5,5-H), 4.76(1H,s,3'-H), 4.80(1H,d,1.5,3-H)
VIII	orange powder, 84–87	1735, 1690, 1665	3.69(3H,s,-COOMe), 4.31(1H,s,5'-H), 4.36(1H,d,1.5,3-H),4 42(1H,d,1.5,5-H)
IX	red needles, 110–112	1735, 1688, 1660	3.70(3H,s,-COOMe),4 26(1H,d,1.6,2-H), 4.28(1H,s,5'-H), 4.26(1H,d,1.6,5-H)
X	red prisms, 109–110	1730, 1680, 1658	3.71(3H,s,-COOMe), 3.77(1H,d,2.4,2-H), 3.98(1H,d,2.4,3-H), 4.50(1H,s,5'-H)
XIa [c,d]	yellow prisms, 92–100	1735	3.32(1H,bs,3'-H), 3.37(3H,s,-COOMe), 3.87(1H,bs,5'-H), 3.88(1H,s,5-H)
XIIa [c,d]	yellow oil	1735	3.36(3H,s,-COOMe), 3.60 and 3.64(each 1H, d,1.4,3',5'-H), 3.65(1H,s,3-H)
XIV	yellow oil	3410	3.69 and 3.79(each 1H,d,1.4,3',5'-H), 3.80(1H,s,3-H)
XV	yellow oil	558	3.40(2H,t,7.0,-CH_2Br), 3.74 and 3.80(each 1H,bs,3',5'-H), 3 80(1H,s,3-H)
XVI	yellow oil	2240	3.71 and 3.80(each 1H,d,1.5,3',5'-H), 3.82(1H,s,3-H)
XVII	red-brown prisms, 190–191	1655	3.41(1H,s,3'-H), 4.24(1H,s,5-H)
XVIII	orange flakes, 202–204	1655	3.80(1H,s,3'-H), 4.54(1H,s,3-H)
XIX	orange prisms, 189–190	1650	3.77(1H,s,5'-H), 3.84(1H,s,3-H)
XX [c]	yellow plates, 111–114	–	2.99(1H,s,3'-H), 3.43(1H,s,5-H) 20.71, 21.78, 22.66, 22.90, 24.02, 24 17, 24.51, 24.75, 24.85, 26.07, 26.85, 26.95, 28.31, 30 16, 34.99 (bridge-C), 69.44, 70.51, 78 16, 82.16, 82.89(2C), 83.28, 83.57, 83.91, 86.49(Cp ring-C)
XXI [c]	yellow crystals, 161–164	–	3.58(2H,s,3,3'-H) 22.07, 22.22, 22.46, 23.88, 27.83, 28.07, 30.21, 35.67(bridge-C), 63.79, 80.31, 82.69, 83.08, 85.08(Cp ring-C)
XXVIII	orange crystals, 106–108	1690	3.80, 4.01, 4.13 and 4.26(each 1H,m,1,2,4,5-H), 4.45 and 4.49(each 1H,d,0.8,2',4'-H)
XXIX	orange-red oil	1685	3.68-3 88(3H,m,1.2.4-H), 4.10(1H,dt,1.4, 2.4,5-H), 4.30 and 4.43(each 1H,2.4,4',5'-H)
XL	orange-red oil	1665	3.89-4.10(4H,m,1,2,4,5-H), 4.31 and 4.39 (each 1H,d,2.5,4',5'-H)
XLV	red oil	1663	3.84 and 3.92(each 1H,dd,1.8,2.5,1,5-H) 3.98(1H,t,1.8,3-H), 4.40(1H,s,3'-H)

[a] The IR spectra were measured in KBr disk and neat liquid on a NaCl plate, respectively, for crystalline and oily compounds. [b] Relative intensities, multiplicities, coupling constants (Hz) and assignments are given in parentheses. [c] The ^1H NMR spectra of XIa and XIIa, and the ^{13}C NMR spectra of XX and XXI were obtained in C_6D_6. [d] Butanoic acids XIb (yellow crystals, m.p. 156–159°C, IR. 1705 cm^{-1}) and XIIb (yellow crystals, m.p. 167–169°C, IR: 1695 cm^{-1}), which were obtained by hydrolysis of XIa and XIIa, respectively, were unstable in solution.

Friedel–Crafts acylation of [4]-α-oxo[3](2,3)[4]ferrocenophane (VII) (348 mg, 1.00 mmol) with succinic anhydride (200 mg, 2.00 mmol) and $AlCl_3$ (533 mg, 4.00 mmol) in dichloromethane (30 ml) was carried out by the same procedure as in the reaction of I. Three compounds, VIII, IX and X, were obtained by column chromatography over silica gel with hexane/acetone (20/1).

Catalytic hydrogenolysis of acyl[4][3][4]ferrocenophanes (IVa, V and VI)

A mixture of acyl[4][3][4]ferrocenophane and PtO_2 (10% of substrate weight) in acetic acid was shaken under hydrogen, at ca. 3.5 atm for 2 days. Benzene was added to the reaction mixture and acetic acid was removed from the organic layer by neutralization with saturated aq. Na_2CO_3 containing ascorbic acid. The benzene layer was washed with saturated aq. NaCl, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over alumina to yield the reduction product.

Hydrolysis of butanoate derivatives (IVa, XIa and XIIa)

A mixture of the methyl butanoate derivative, ethanol and 20% aq. NaOH was stirred at 80°C for 10 min followed by neutralization with 6 *N* HCl. The benzene extracts were washed with saturated aq. NaCl, dried over Na_2SO_4 and evaporated.

Synthesis of [4][3][4]ferrocenophanebutanoate (XIIa) by an alternative route

An ether solution (30 ml) of 5-[4][3][4]ferrocenophanepropanoate (XIII) [16] (830 mg, 1.91 mmol) was added dropwise to a suspension of $LiAlH_4$ (300 mg, 6.25 mmol) in ether (50 ml) at 0°C, and the reaction mixture was stirred at room temperature for 2 h. After hydrolysis of the mixture with wet ether, the ether layer was separated, washed with saturated aq. $NaHCO_3$ and saturated aq. NaCl, dried over Na_2SO_4, and evaporated. The residue was column-chromatographed over alumina with ethyl acetate to give the propanol derivative (XIV) (669 mg, 90%).

PBr_3 (1.2 g, 4.4 mmol) was added dropwise to a solution of the alcohol XIV (685 mg, 1.75 mmol) in dry benzene (20 ml) containing pyridine (1 ml) at 0°C under nitrogen. The reaction mixture was stirred at 70°C for 2 h, and then ethanol was added, followed by the addition of water to decompose the reagent. The benzene extracts were washed with saturated aq. $NaHCO_3$ and aq. NaCl, dried over Na_2SO_4 and evaporated. The crude product was column-chromatographed over alumina, and the bands eluted with benzene and ethyl acetate yielded, respectively, bromide XV (282 mg, 38%) and the starting material (211 mg, 31%).

A solution of the bromide XV (377 mg, 0.829 mmol) in dry acetonitrile (5 ml) was added dropwise to a mixture of dry KCN (500 mg, 7.69 mmol) and acetonitrile (3 ml). After 18-crown-6 (100 mg) had been added, the reaction mixture was refluxed under nitrogen for 6 h. Water and benzene were added and the resulting organic layer was washed with saturated aq. NaCl, dried over Na_2SO_4 and evaporated. The crude product was column-chromatographed over alumina, and the band with benzene/ethyl acetate (30/1) yielded cyanide XVI (316 mg, 95%).

The cyanide XVI (207 mg, 0.516 mmol) was dissolved in heated ethanol (10 ml), and 10% aq. NaOH (30 ml) was added to the solution. The mixture was refluxed for 6 h, and then neutralized with 6 *N* HCl. The benzene extracts were washed with saturated aq. NaCl, dried over Na_2SO_4 and evaporated. A solution of diazomethane in ether was added to a solution of the above residue in benzene, and the solvent was evaporated. The crude product was column-chromatographed over alumina with

hexane/ethyl acetate (10/1), separating into two bands which yielded methyl 5-[4][3][4]ferrocenophanebutanoate (102 mg, 45%) and the starting material (XVI, 71 mg, 34%). The ester was completely identical to compound XIIa derived via acylation of I.

Cyclization of [4][3][4]ferrocenophanebutanoic acids (XIb and XIIb)

To a solution of the butanoic acid derivative and dry triethylamine in freshly distilled dichloromethane was added dropwise a solution of ethyl chlorocarbonate in dichloromethane at 0°C under nitrogen, and the mixture was stirred at 0°C for 30 min. Under degassed conditions *, $AlCl_3$ was added to the above solution. The molar ratio of the substrate to reagents used in this reaction was 1/1.2/1.5/2.7 for butanoic acid/NEt_3/$ClCO_2Et$/$AlCl_3$. The reaction mixture was stirred at room temperature for 1 h, and quenched by ice-water containing ascorbic acid. The dichloromethane extracts were washed with saturated aq. NaCl, dried over $CaCl_2$ and evaporated. The residue was chromatographed over thin-layered silica gel on a preparative scale with benzene/acetone (30/1).

Reduction of ketones (XVII, XVIII and XIX)

$LiAlH_4$ powder was suspended in a dry ether solution of $AlCl_3$. A solution of ketone in dry ether was added dropwise to the suspension. After stirring for 2 h, moist ether and then water were added to the reaction mixture. The resulting hydrolysate was extracted with ether. The extracts were washed with aq. NaCl, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over alumina with hexane/acetone (40/1).

Treatment of ferrocenophanes with $AlCl_3$

A mixture of the corresponding ferrocenophane (0.15–0.20 mmol) and $AlCl_3$ (10 mol equiv. to the substrate) in dichloromethane (10 ml) was stirred under nitrogen at room temperature. The reaction of XXX and XXXII was carried out under degassed conditions *, because the compounds are very sensitive to air when in a solution containing $AlCl_3$. The reaction mixture was poured into ice-water containing ascorbic acid, and the dichloromethane extracts were washed with saturated aq. NaCl, dried over $CaCl_2$ and evaporated. The residue was chromatographed over silica gel or thin-layered silica gel on a preparative scale to yield the rearrangement products and/or the recovered starting material. The products VII, XXX–XXXII [3] and XLII [28] yielded compounds which were identical to authentic samples. The characterization of the new compounds, XXVIII, XXIX, XL and XLV, is summarized in Table 2.

Acknowledgements

The authors are grateful to Dr. Saito of Tanabe Seiyaku Co. Ltd. for elemental analyses, and Mrs. H. Hasegawa and Miss N. Sawabe of this Faculty for measurement of the mass spectra and NMR spectra, respectively.

* The reaction was carried out in a Schlenk tube connected with a vacuum system.

References

1 M. Hisatome, Y. Kawajiri, K. Yamakawa, K. Kozawa and T. Uchida, J. Organomet. Chem., 236 (1982) 359.
2 M. Hisatome, T. Sakamoto and K. Yamakawa, J. Organomet. Chem., 107 (1976) 87.
3 M. Hisatome, N. Watanabe, T. Sakamoto and K. Yamakawa, J. Organomet. Chem., 125 (1977) 79.
4 M. Hisatome, Y. Kawajiri, K. Yamakawa and Y. Iitaka, Tetrahedron Lett., (1979) 1777.
5 M. Hisatome and M. Hillman, J. Organomet. Chem., 212 (1981) 217.
6 M. Hisatome, Y. Kawajiri and K. Yamakawa, J. Organomet. Chem., 226 (1982) 71.
7 M. Hisatome, Y. Kawajiri, K. Yamakawa, K. Mamiya, Y. Harada and Y. Iitaka, Inorg. Chem., 21 (1982) 1345.
8 M. Hisatome, Y. Kawajiri, K. Yamakawa, Y. Harada and Y. Iitaka, Tetrahedron Lett., 23 (1982) 1713.
9 M. Hisatome, N. Watanabe and K. Yamakawa, Chem. Lett., (1977) 743.
10 M. Hisatome, J. Watanabe and K. Yamakawa, J. Organomet. Chem., 266 (1984) 159.
11 M. Hillman, B. Gordon, A.J. Weiss and A.P. Guzikowski, J. Organomet. Chem. 155 (1978) 77.
12 M. Hillman and E. Fujita, J. Organomet. Chem., 155 (1978) 99.
13 F. Vögtle and P. Neumann, Tetrahedron, 26 (1970) 5847.
14 K.L. Rinehart, Jr., R.J. Curby, Jr., D.H. Gustafson, K.G. Harrison, R.E. Bozak and D.E. Bublitz, J. Am. Chem. Soc., 84 (1962) 3263.
15 M. Rosenblum, A.K. Banerjee, N. Danieli, R.W. Fish and V. Schlatter, J. Am. Chem. Soc., 85 (1963) 316.
16 M. Hisatome, J. Watanabe, K. Yamakawa, K. Kozawa and T. Uchida, J. Organomet. Chem., 262 (1984) 365.
17 Our unpublished results.
18 J.D. Dunitz, L.E. Orgel and A. Rich, Acta Crystallogr., 9 (1956) 373.
19 D.W. Slocum, S.P. Tucker and T.R. Engelman, Tetrahedron Lett., (1970) 621.
20 D.E. Bublitz, J. Organomet. Chem., 16 (1969) 149.
21 T.D. Turbitt and W.E. Watts, J. Chem. Soc., Perkin Trans. 2, (1974) 189.
22 D.T. Hefelfinger and D.J. Cram, J. Am. Chem. Soc., 93 (1971) 4754.
23 H. Horita, N. Kannen, T. Otsubo and S. Misumi, Tetrahedron Lett., (1974) 501.
24 C.A. Buehler and D.E. Pearson, Survey of Organic Syntheses, Wiley-Interscience, New York, 1970, p.653.
25 (a) R.O.C. Norman and R. Taylor, Electrophilic Substitution in Benzenoid Compounds, Elsevier, Amsterdam, 1965, p.174; (b) N.L. Allinger, M.P. Cava, D.C. De Jongh, C.R. Johnson, N.A. Lebel and C.L. Stevens, Organic Chemistry, Worth, New York, 1971, p.358.
26 (a) I. Agranat, Y.-S. Shih and Y. Bentor, J. Am. Chem. Soc., 96 (1974) 1259; (b) I. Agranat, Y. Bentor and Y.-S. Shih, J. Am. Chem. Soc., 99 (1977) 7068.
27 (a) P.H. Gore, Chem. Ind., (1974) 727; (b) A.D. Andreou, P.H. Gore and D.F.C. Morris, J. Chem. Soc., Chem. Commun., (1978) 271.
28 K.L. Rinehart, Jr., D.E. Bublitz and D.H. Gustafson, J. Am. Chem. Soc., 85 (1963) 970.