Journal of Organometallic Chemistry, 248 (1983) 107–122
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STEREOCHEMISTRY OF THE REACTION OF GRIGNARD REAGENTS WITH 3-ARYL- AND 3-ALKYL-[5]FERROCENOPHANE-1,5-DIONES

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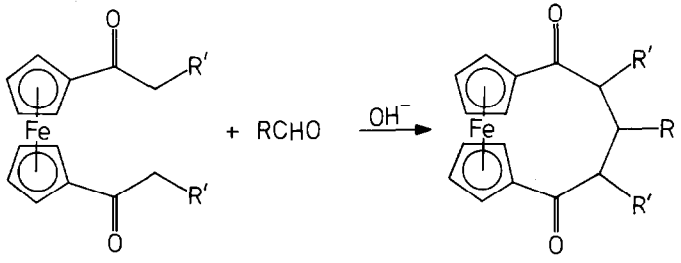
(Received November 12th, 1982)

Summary

The reaction of Grignard reagents with 3-aryl- and 3-alkyl-[5]ferrocenophane-1,5-diones is completely stereospecific giving exclusively derivatives in which the introduced alkyl groups are *cis* to substituents at C(3). The chair conformation, with strong intramolecular hydrogen bonding, predominates in the hydroxyketones obtained, and this is the only conformer present in the case of the dihydroxy derivatives. The second isomer of the hydroxyketones is also the *cis* type, but its bridge has a twist conformation.

Introduction

We have previously reported [1] that the reaction of diacetylferrocene with aldehydes in a wet DMSO solution of KOH at elevated temperature leads to good yields of [5]ferrocenophane-1,5-diones with aryl or alkyl substituents at the third bridge carbon (Scheme 1). The C(2) and C(4) substituted derivatives were obtained



SCHEME 1

when other 1,1′-diacylferrocenes were used instead of 1,1′-diacetylferrocene. Several reports dealing with [5]ferrocenophane derivatives having one or two substituents at the mentioned positions have been published [2–9], but there is only one paper describing 1,5-dialkyl derivatives [10]. To our knowledge, there are no reports dealing with 1,3,5-trialkyl or mixed alkyl-aryl derivatives of [5]ferrocenophane.

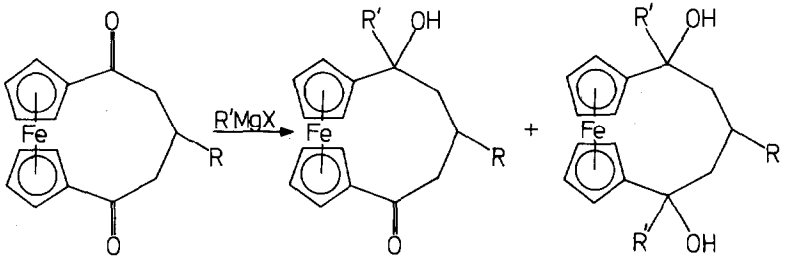
0022-328X/83/$03.00

Derivatives having alkyl groups at the terminal bridge carbon atoms are needed for the study of steric effects of substituents at the bridge on acylation of ferrocenophanes (compare ref. 11). Reaction of readily available [5]ferrocenophane-1,5-diones [1] with Grignard reagents was chosen as the simplest way to these compounds.

There are several papers dealing with Grignard reactions of acylferrocenes [12–19], but we have not been able to find any example of this reaction with ferrocenophanes. Since the [5]ferrocenophane-1,5-diones used as the substrates had usually a substituent at C(3), stereochemical problems arose, and in this paper we describe the results of our studies on stereochemistry of the products.

Results and discussion

Grignard reactions carried out on [5]ferrocenophane-1,5-diones are shown in Scheme 2. Usually both hydroxyketone I (and II, vide infra) and diol III were



SCHEME 2

isolated chromatographically from the same reaction mixture, and the ratio of these products shown to depend only on reaction conditions (relative amounts of reactants, reaction time). In some experiments, when R was t-butyl or isopropyl, only compound I was isolated. In these cases steric hindrance by the first bulky substituent protected the remaining carbonyl group to some extent against attack by the second molecule of the Grignard reagent. The results from several experiments are listed in Table 1.

It is well known that ferrocenyl carbinols readily undergo dehydration to olefins [20–23]. This reaction lowered the yields of products and complicated the separation of the products. Another side reaction was reduction of the ketone function of the substrate to a hydroxy group by the Grignard reagent [24]. To minimize these disadvantages, an excess of the Grignard reagent was used and the work-up was modified to avoid the presence of acids which catalyse the dehydration. Nevertheless, the yields of products were not high, and products of dehydration and reduction were isolated in some instances.

The five-membered bridge of the [5]ferrocenophane system can exist in two possible conformations: a chair and a twist form (Fig. 1). The latter is preferred, and has been found in all the investigated molecules of this type [1,24–26]. To our knowledge, the chair form has never been detected, but it is reasonable to assume that special structural effects could force the molecule into this conformation.

TABLE 1

CONDITIONS USED FOR THE REACTION OF [5]FERROCENOPHANE-1,5-DIONES WITH GRIGNARD REAGENTS, AND YIELDS OF PRODUCTS

R	R'MgX	Ratio of reagents R'MgX/dione (mol/mol)	Reaction time (min)	Yield (I+II) (%)	Yield III (%)
Ph	CH_3MgCl	1.5	10	22	21
Ph	CH_3MgCl	5.0	120	1.3	80
Ph	CH_3CH_2MgI	9.0	10	20	44
Ph	CH_3CH_2MgI	12.0	300	9	64
Ph	$CH_3CH_2CH_2I$	9.0	15	24	14
Ph	$(CH_3)_2CHMgI$	2.0	10	15	0
Ph	$(CH_3)_2CHMgI$	9.0	300	3	38
Ph	$CH_2{=}CHCH_2MgI$	9.0	300	0	27
Ph	$(CH_3)_3CMgCl$	9.0	300	35	36
Ph	$(CH_3)_3CMgCl$	5.0	30	15	0
p-$CH_3OC_6H_4$	$(CH_3)_3CMgBr$	9.0	60	49	0
$(CH_3)_2CHCH_2$	CH_3CH_2MgI	4.5	10	28	5
CH_3CH_2	CH_3CH_2MgI	4.5	10	15	6

In several instances two isomers of 1,3-disubstituted 5-hydroxy[5]ferrocenophan-1-one (I and II) were isolated. The first difference observed between them was in the rates of elution from a column during the chromatography. The rapidly eluted isomer (I) was more soluble in ordinary solvents and its IR spectrum showed a very strong intramolecular hydrogen bond. The C=O and O–H stretching bands observed at ν1620 and ~ 3500 cm^{-1}, respectively, in the spectrum of the solid or concentrated solution shifted only slightly on dilution (Fig. 2). This value (3500 cm^{-1}) is typical for strong intramolecular hydrogen bonding of the type O–H · · · O=C, and has been found previously in the spectra of α- and γ-hydroxyketones [27] and of 1-acetyl-1′-α-hydroxyferrocene [28]. On the other hand, the IR spectra of isomer II

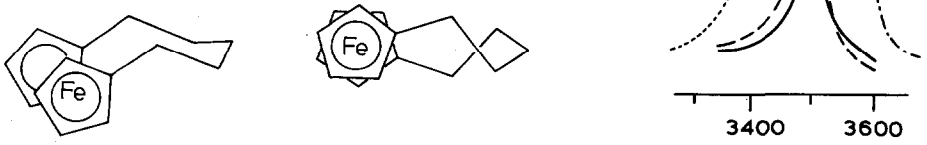


Fig. 1. Conformational forms of [5]ferrocenophane.

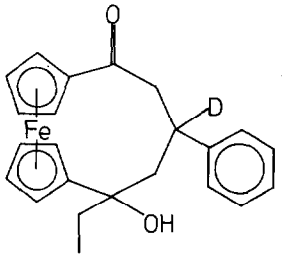
Fig. 2. O–H Stretching bands in the IR spectra of: ——— Ib - HCB mull; — — — Ib - 0.0017 *M* solution in CCl_4, *d* 20 mm; · · · · · · IIb - HCB mull; –·–·–· IIb - 0.0017 *M* solution in CCl_4, *d* 20 mm.

revealed only an intermolecular hydrogen bond with ν(C=O) ~ 1650 and ν(O–H) ~ 3430 cm^{-1} in a solid state. In this case the O–H stretching band is shifted to ~ 3550 cm^{-1} in a diluted CCl_4 solution, indicating intramolecular hydrogen bonding with the Fe atom [29–32].

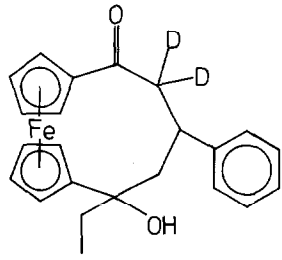
The NMR spectra of isomers I and II are different but the alkyl group resonances lie in a similar region. For example, when R = Ph and R′ = Et, the ethyl CH_2 group appears as a quartet at δ 1.44 and the CH_3 group as a triplet at δ 0.55 in the spectrum of isomer I, and the values for isomer II are 1.46 and 0.65 ppm, respectively. The remarkable shift of these resonances from their normal positions to a higher field must be caused by the location of the alkyl group in the shielding zone of the ferrocene moiety, i.e. above the cyclopentadienyl ring [33].

An examination of Dreiding models of I indicates two geometries of the molecule which are consistent with the spectroscopic properties of isomers I and II. All the other theoretically possible structures must be rejected because of the steric interaction between substituents. As it can be seen from Fig. 3, both isomers possess the same *cis* arrangement of substituents (alkyl and phenyl) and differ only in conformation of the bridge. There must be an unusually high barrier to rotation between the conformers, since we have never observed any transformation of one into the other during the recrystallization, even from such polar solvents as alcohol or THF.

Final confirmation of the structures of isomers I and II was available from an

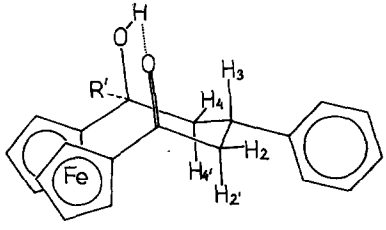


IV

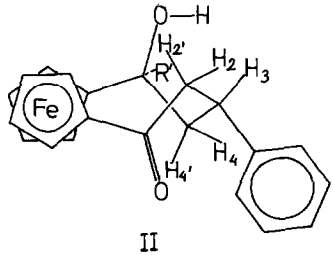


V

analysis of the ring methylene resonances in their NMR spectra (Fig. 4). In order to simplify the problem, two deuterium labelled derivatives (IV and V) were synthesized. Deuterium incorporation, as shown by spectroscopy, was 54% in compound IV and 75% in compound V.



I



II

Fig. 3. Molecular geometries of isomers I and II.

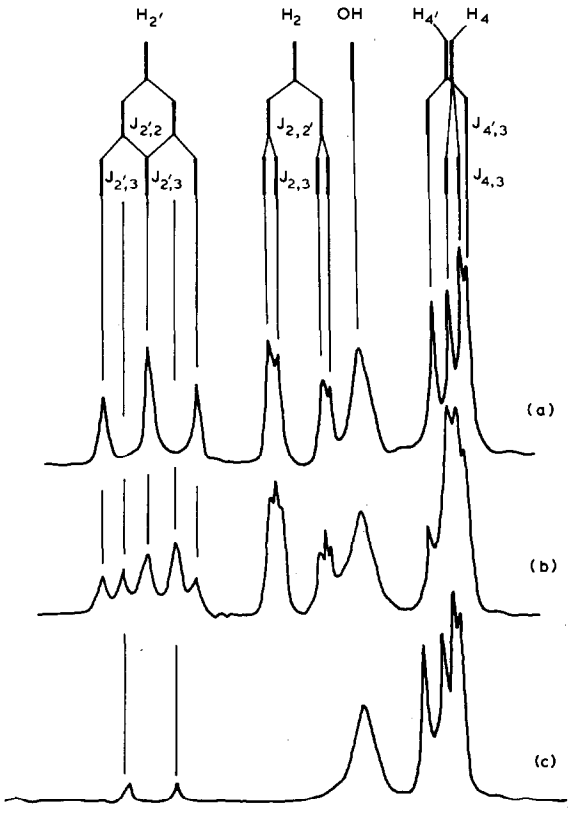


Fig. 4. Ring methylene signals of: (a) compound Ib (see Table 2); (b) 54% of compound IV in the mixture with Ib; (c) 75% of compound V in the mixture with partly deuterated species.

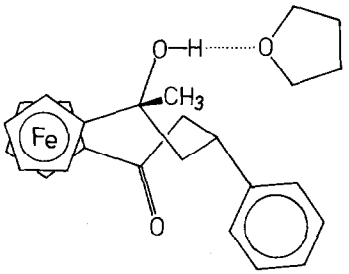
The more deshielded methylene protons are those adjacent to the carbonyl group (H(2) and H(2')). Their splitting pattern may be considered as an AB part of the ABX system with $J_{22'}$ 13.5 Hz, $J_{2',3}$ 13.0 Hz and $J_{2,3}$ 3.2 Hz. The closeness of the values of $J_{2',3}$ and $J_{2,2'}$ is the reason why $H_{2'}$ is seen as a triplet. The given values indicate that $H_{2'}$ is located *trans* and H_2 *cis* to H_3, in accordance with previous findings for cyclohexane derivatives having rigid rings [34–35]. The bridge in the molecule of I must also be rigid.

The signals due to the C(4) protons appear further upfield, at approximately δ 2.2–2.3 ppm, as two doublets. This splitting can be interpreted as an AB part of the ABX proton system with $\delta(A) \approx \delta(B)$. The coupling constants (J 14 and 3 Hz) indicate that the first of the protons is located *trans* and the other *cis* to that at C(3). These data also confirm the structure of I.

Quite a different situation is observed in the case of isomers II. Their NMR spectra reveal only two doublets due to the methylene groups of the bridge, which became singlets for species deuterated at C(3) (IV). For example, when R = Ph, R' = Et (IIb), the doublet from the protons at C(2) appears at δ 2.96 ppm (J 7.5 Hz) and that from the protons at C(4) at δ 2.19 (J 7.5 Hz). This can be attributed to the flexibility of the molecule. Similar observations have been made previously on the

NMR spectra of 3-alkyl[5]ferrocenophane-1,5-diones in which the bridges also exist in the twist conformation [36].

An interesting adduct was obtained after crystallization of IIa from a hexane/THF mixture (2/1). This adduct, VI separates as grainy red crystals and is relatively

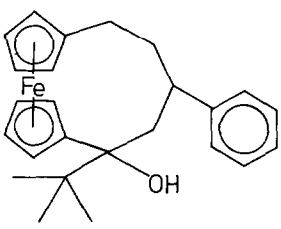


VI

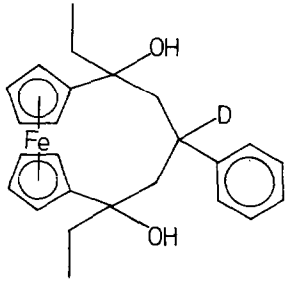
stable (m.p. 152°C). Its IR spectrum is different from that of isomer II, especially in the O–H stretching region, and exhibits two broad bands with maxima approximately at 3320 and 3450 cm^{-1} (in HCB mull). This indicates formation of a new intermolecular hydrogen bond between the O–H group of II and the oxygen atom of THF. The NMR spectrum is unchanged in $CDCl_3$ solution, except for the presence of the signals from THF. Crystallization of II from ethanol did not give an adduct. No attempts were made to prepare other adducts similar to VI.

Turning now to consideration of the structure of dihydroxy derivatives III, we find that their IR spectra show strong intramolecular hydrogen bonding; e.g. two strong broad bands with maxima at 3265 and 3428 cm^{-1} are observed in the spectrum of IIIb taken as an 0.0017 *M* solution in CCl_4. The first band is also observed in the spectrum of the solid and is probably attributable to intermolecular hydrogen bonding [37].

Further support for the presence of an intramolecular hydrogen bond in III can be obtained from comparison of the IR spectrum of III (R = Ph, R′ = t-Bu) with that of compound VII. Because of steric crowding, molecules of VII are unable to



VII



VIII

form an intermolecular hydrogen bond, and only one band is observed at 3610 cm^{-1}, corresponding to free OH stretching vibrations, even in the solid. For the same reasons intermolecular hydrogen bonding cannot occur between molecules of compound III, in the case when R′ = t-Bu, and the intramolecularly bonded hydroxyl groups give O–H stretching bands at about 3420 cm^{-1} (HCB mull).

Examination of the Dreiding model of the molecule of diol III indicates that the

only possible structure in which hydrogen bonding can take place between the hydroxyl groups is that represented in Fig. 5, with the bridge in the chair form. The alkyl and phenyl groups have a *cis-cis* configuration. This is in agreement with the observation from the NMR spectrum that both alkyl groups, at C(1) and C(5), are magnetically equivalent, and are shielded by the ferrocene system and shifted upfield. When R = Ph, R′ = Et (compound IIIb) a triplet appears at δ 0.61 and a quartet at 1.49 ppm.

Analysis of the bridge proton resonances of III (Fig. 6) supports the proposed structure. The methylene group protons may be treated as an AB part of the ABX type system because of the symmetry of the molecule. The obtained values of coupling constants $J_{AX} = 10$ Hz and $J_{BX} = 2$ Hz reveal that the H(A) and H(B) protons are situated *trans* and *cis* to H(X), respectively. The H(A) atoms resonate at lower field than the H(B) atoms because the latter lie outside the molecule and are shielded by the phenyl and cyclopentadienyl rings. These assignments are confirmed by the spectrum of a deuterium labelled version of III (compound VIII).

We conclude that bridges of the [5]ferrocenophane system can exist in the more strained chair conformation when there are strong attractive interactions between their substituents. In the case of 1,5-dihydroxy or 1,5-ketohydroxy derivatives these are hydrogen bondings between oxygen atoms. Alkyl substituents introduced into

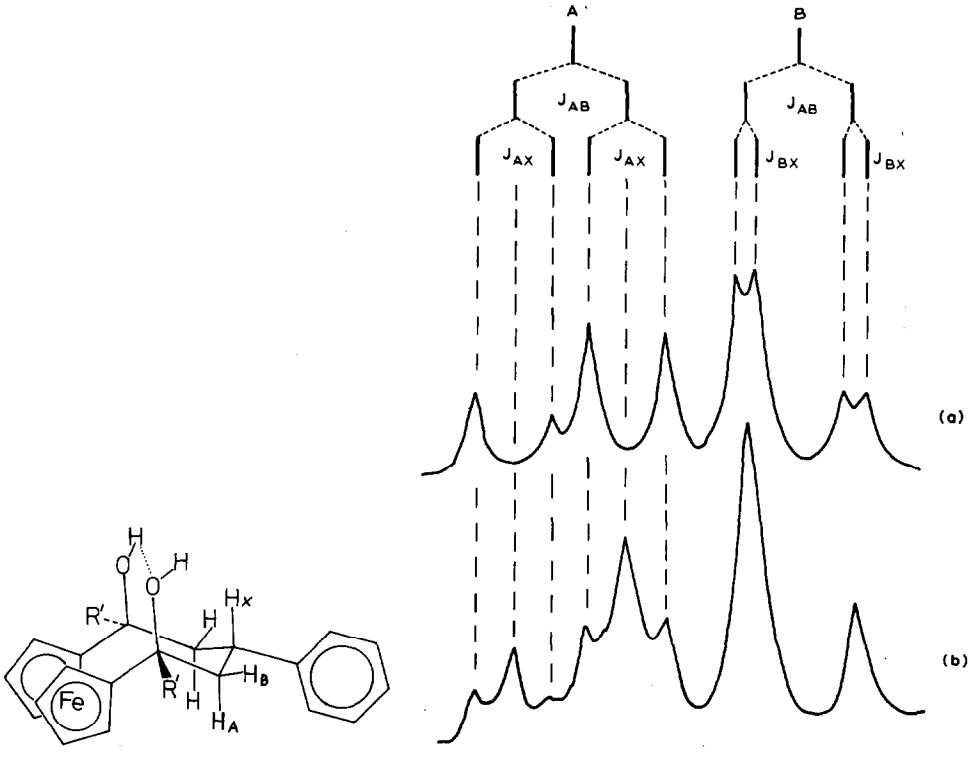
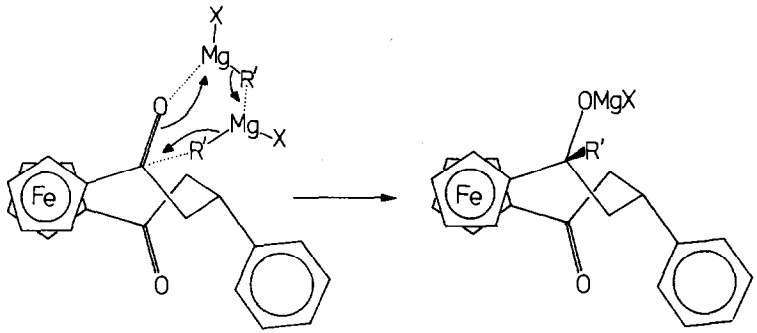


Fig. 5. Molecular structure of diols III.

Fig. 6. Bridge methylene proton resonances of: (a) IIIb; (b) mixture of 54% VIII and 46% IIIb.

the molecule of 3-aryl- or 3-alkyl-[5]ferrocenophane-1,5-dione in the Grignard reaction are located *cis* to the C(3) groups.

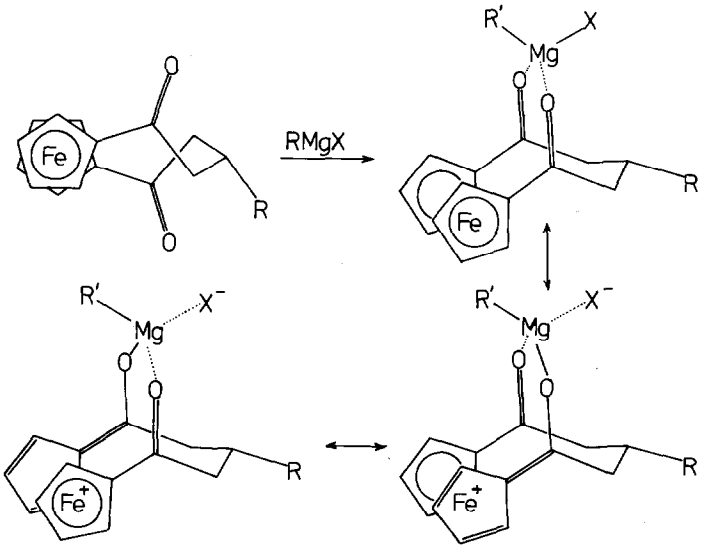
How can this stereoselectivity be explained? If an attack of the Grignard reagent takes place on the carbonyl group of the molecule in its usual twist (or opposed [24]) conformation, it seems to approach from the less hindered side, producing only *cis* isomer II (Scheme 3). Attack at another side involving formation of the OMgX



SCHEME 3

group in the space occupied by the substituent at C(3).

The route to the main product, isomer I, seems to be quite different. Complexation of the magnesium atom of the Grignard reagent by the carbonyl groups in the first step must stabilize the chair conformation of the molecule; this is very likely because of the strong electron-donating properties of the ferrocene system [38–40], which will cause considerable stabilization of the complex (Scheme 4). For the same



SCHEME 4

reasons, the carbonyl carbon atoms in the molecule of [5]ferrocenophane-1,5-dione are not electron deficient and have less electrophilic character than is usual in ketones. Attraction of electrons from the carbonyl groups by the magnesium atom

make them more susceptible to attack by another molecule of the Grignard reagent. As a result, the *cis* stereochemistry of the reaction is observed. Similar explanations have been given by Canonne et al. for stereoselectivity of the reaction of 1,1'-diacylferrocene with Grignard reagents [41].

The product ratio (II/I) depends mainly on the nature of the Grignard reagent, in the case R = Ph, changes from ca. 3/2 (MeMgCl) through 2/3 (EtMgI) to 0/1 for i-PrMgI, t-BuMgCl. In the case of bulky Grignard reagents, the formation of the product is slower than is the complexation.

Experimental

Melting points are uncorrected. The ^1H NMR spectra were recorded on Tesla BS 80 MHz or JEOL 100 MHz spectrometers at ambient temperature. The spectra were taken in $CDCl_3$ with tetramethylsilane as internal standard. IR spectra were recorded on a Zeiss UR-10 instrument. Mass spectra were processed by Dr. K. Nagraba with a LKB-9000S mass spectrometer at 70 eV in the Regional Laboratory of Physico-Chemical Analyses and Structural Research in Krakow.

Column chromatography was carried out using Merck silica gel 60–200 mesh. Ether was dried by storage over KOH and 4A molecular sieves. Alkyl halides were purified before use by distillation from phosphorus pentoxide. Methyl magnesium chloride was a commercial 20% solution in THF-Merck; other Grignard reagents were synthesized immediately before use. 3-Alkyl- and 3-aryl-[5]ferrocenophane-1,5-diones were obtained as previously described [1].

Reaction of [5]ferrocenophane-1,5-diones with Grignard reagents. General procedure

The Grignard reagent prepared from magnesium metal turnings (4.8 g, 200 mmol) and alkyl halide (100 mmol) in anhydrous ether (100 ml) was added to a vigorously stirred suspension of [5]ferrocenophane-1,5-dione in 100 ml of dry ether under nitrogen.

After the time shown in Table 1, the mixture was poured on to crushed ice (200 g) and a saturated solution of sodium bicarbonate (50 ml) was added. The organic layer was separated and dried ($MgSO_4$) and the solvent was removed on a rotatory evaporator to leave a semi-solid. Column chromatography over 60 g of silica gel with benzene/chloroform/ethyl acetate (5/5/1) as the eluent gave, in order of elution: hydroxyketone I, diol III and hydroxyketone II. Sometimes, reduction and dehydration products were also isolated. Data for the obtained compounds are listed in Table 2 and Table 3.

Deuterium-labelled compounds IV and VIII

Deuterium-labelled benzaldehyde obtained from the reaction of benzonitrile with $SnCl_2$ and DCl was used to produce 3-deuterio-3-phenyl[5]ferrocenophane-1,5-dione. Its mass spectrum indicated that deuterium incorporation was 54%. Reaction of this substance with ethylmagnesium iodide carried out in the usual manner gave IV and VIII. Two isomers of IV were isolated. The melting points of the labelled compounds were the same as those of ordinary Ib, IIb and IIIb. Mass spectrum of IV: ($C_{23}H_{23}DFeO_2$) *m/e*: 391 (3.6), 390 (20), 389 (60, M^+), 388 (47), 255 (100).

(Continued on p. 121)

TABLE 2

ANALYSES, MELTING POINTS AND SOLVENTS FOR CRYSTALLIZATION OF COMPOUNDS I, II, III

Compound			Molecular formula	Analyses (Found(calcd.) (%))		M.p. (°C)	Solvent
	R	R′		C	H		
Ia	C_6H_5	CH_3	$C_{22}H_{22}FeO_2$	70.92 (70.60)	6.32 (5.93)	162–164	n-hexane/THF
Ib	C_6H_5	CH_2CH_3	$C_{23}H_{24}FeO_2$	71.00 (71.15)	6.33 (6.23)	196–198	n-hexane/benzene
Ic	C_6H_5	$CH_2CH_2CH_3$	$C_{24}H_{26}FeO_2$	71.92 (71.65)	6.62 (6.51)	197–198	n-hexane/THF
Id	C_6H_5	$CH(CH_3)_2$	$C_{24}H_{26}FeO_2$	71.47 (71.65)	6.70 (6.51)	206–207	n-hexane/THF
Ie	C_6H_5	$C(CH_3)_3$	$C_{25}H_{28}FeO_2$	71.91 (72.12)	6.94 (6.78)	227–229	dioxane/isopropanol
If	p-$CH_3OC_6H_4$	$C(CH_3)_3$	$C_{26}H_{30}FeO_3$	70.31 (69.96)	7.18 (6.77)	226–228	toluene
Ig	$CH_2CH(CH_3)_2$	CH_2CH_3	$C_{21}H_{28}FeO_2$	68.72 (68.48)	7.47 (7.66)	136–137	n-hexane/benzene

IIa	C_6H_5	CH_3	$C_{22}H_{22}FeO_2$	70.85 (70.60)	6.22 (5.93)	163–165	ethanol/water
IIb	C_6H_5	CH_2CH_3	$C_{23}H_{24}FeO_2$	71.45 (71.15)	6.42 (6.23)	134–135	n-hexane/benzene
IIc	C_6H_5	$CH_2CH_2CH_3$	$C_{24}H_{26}FeO_2$	71.24 (71.65)	6.53 (6.51)	146–148	n-hexane/benzene
IIg	$CH_2CH(CH_3)_2$	CH_2CH_3	$C_{21}H_{28}FeO_2$	68.53) (68.48)	7.96 (7.66)	136–137	n-hexane/benzene
IIIa	C_6H_5	CH_3	$C_{23}H_{26}FeO_2$	70.52 (70.78)	6.98 (6.71)	181–183	n-hexane/toluene
IIIb	C_6H_5	CH_2CH_3	$C_{25}H_{30}FeO_2$	71.91 (71.71)	7.09 (7.22)	182–183	n-hexane/acetone
IIIc	C_6H_5	$CH_2CH_2CH_3$	$C_{27}H_{34}FeO_2$	72.30 (72.64)	7.77 (7.68)	182–184	n-hexane/benzene
IIId	C_6H_5	$CH(CH_3)_2$	$C_{27}H_{34}FeO_2$	72.56 (72.64)	7.64 (7.68)	196–198	n-hexane/benzene
IIIe	C_6H_5	$C(CH_3)_3$	$C_{29}H_{38}FeO_2$	73.78 (73.41)	8.32 (8.07)	203–204	n-hexane/toluene
IIIg	$CH_2CH(CH_3)_2$	CH_2CH_3	$C_{23}H_{34}FeO_2$	69.52 (69.34)	8.84 (8.60)	151–152	n-hexane
IIIh	C_6H_5	$CH_2CH{=}CH_2$	$C_{27}H_{30}FeO_2$	73.70 (73.30)	6.86 (6.84)	123–125	n-hexane/benzene

TABLE 3

SPECTROSCOPIC DATA FOR COMPOUNDS I, II AND III

Compound	NMR δ (ppm)			IR ν [cm^{-1}]			Mass spectra m/e (rel.int., assignment)
	CH_3	Bridge CH_2 (J(Hz))	Ferrocene	O–H	C=O	Solvent	
Ia	1.21 (s, 3 H)	2.16–2.36 (m, 2 H)	4.18 (m, 3 H)	3480	1617	HCB	374 (81, M^+)
		2.69 (dd, 1 H)	4.55 (m, 2 H)				372 (9)
		(14 and 3)	4.68 (m, 1 H)				356 (100, $M^+ - H_2O$)
		3. 25 (dd, 1 H)	4.82 (m, 1 H)				354 (17)
		(14 and 13	5.18 (m, 1 H)				269 (18)
Ib	0.54 (t, 3 H)	2.21 (m, 2 H)	4.18 (m, 3 H)	3500	1624	$CHCl_3$	388 (100, M^+)
		2.70 (dd, 1 H)	4.52 (m, 2 H)				370 (81, $M^+ - H_2O$)
		(13.5 and 3)	4.70 (m, 1 H)				262 (18)
		3.20 (dd, 1 H)	4.82 (m, 1 H)				255 (57)
		(13.5 and 13)	5.07 (m, 1 H)				237 (13)
Ic	0.66 (t, 3 H)	2.15–2.35 (m, 2 H)	4.22 (m, 3 H)	3468	1621	Nujol	402 (21, M^+)
		2.73 (dd, 1 H)	4.58 (m, 2 H)				384 (100, $M^+ - H_2O$)
		(13.5 and 3)	4.74 (m, 1 H)				291 (9)
		3.24 (dd, 1 H)	4.86 (m, 1 H)				277 (12)
		(13.5 and 13)	5.11 (m, 1 H)				
Id	0.62 (d, 6 H)	2.25 (m, 2 H)	4.22 (m, 2 H)	3498	1618	KBr	402 (51, M^+)
		2.73 (dd, 1 H)	4.33 (m, 1 H)	3364			359 (27)
		(13.5 and 2.5)	4.58 (m, 1 H)				256 (14)
		3.27 (t, 1 H)	4.66 (m, 1 H)				255 (73)
		(14)	4.77 (m, 1 H)				199 (14)
			4.90 (m, 1 H)				145 (16)
			5.17 (m, 1 H)				131 (100)
Ie	0.72 (s, 9 H)	2.24–2.38 (m, 2 H)	4.22 (m, 2 H)	3530	1620	HCB	416 (54, M^+)
		2.69 (dd, 1 H)	4.36 (m, 1 H)				361 (19)
		(13.5 and 3)	4.63 (m, 2 H)				360 (56)
		3.16 (t, 1 H)	4.78 (m, 1 H)				256 (16)
			4.90 (m, 1 H)				255 (75)
			5.20 (m, 1 H)				131 (100)

If	0.72 (s, 9 H)	2.24–2.38 (m, 2 H) 2.55 (dd, 1 H) (13.5 and 3) 3.16 (t, 1 H) (13.5)	4.24 (m, 2 H) 4.38 (m, 1 H) 4.55 (m, 1 H) 4.68 (m, 1 H) 4.77, 4.85, 5.14 (m, 1 H)	3550	1622	HCB	446 (14, M^+) 389 (26) 256 (19) 255 (100)
Ig	0.61 (t, 3 H) 0.96 (d, 3 H) 1.01 (d, 3 H)	1.80 (m, 2 H) 2.58 (m, 2 H)	412 (m, 3 H) 4.44 (m, 1 H) 4.52 (m, 1 H) 4.64, 4.74, 4.99 (m, 1 H)	3500	1622	Nujol	368 (89, M^+) 350 (100, $M^+ - H_2O$) 339 (26) 229 (16) 228 (11)
IIa	1.29 (s, 3 H)	2.31 (d, 2 H, 6.5) 2.97 (d, 2 H, 7.5)	3.99 (m, 3 H) 4.44 (m, 2 H) 4.59 (m, 2 H) 4.97 (m, 1 H)	3300– 3600	1650	HCB	374 (11, M^+) 356 (100, $M^+ - H_2O$) 264 (15) 252 (17)
IIb	0.65 (t, 3 H)	2.19 (d, 2 H, 7) 2.98 (d, 2 H, 7.5)	4.21 (m, 3 H) 4.52 (m, 2 H) 4.66 (m, 2 H) 4.94 (m, 1 H)	3400– 3620	1652	$CHCl_3$	388 (22, M^+) 370 (100, $M^+ - H_2O$) 265 (17) 263 (13)
IIc	0.75 (t, 3 H)	2.22 (d, 2 H, 7) 2.99 (d, 2 H, 7.5)	4.20 (m, 3 H) 4.42 (m, 2 H) 4.56 (m, 2 H) 4.96 (m, 1 H)	3530 3400	1650	Nujol	402 (60, M^+) 384 (96, $M^+ - H_2O$) 255 (52) 131 (100)
IIg	0.73 (t, 3 H)	2.00–3.00 (m, 4 H)	3.87–5.00 (m, 8 H)	3390	1650	HCB	368 (22, M^+) 350 (100, $M^+ - H_2O$)
IIIa	1.32 (s, 6 H)	2.00–2.69 (m, 4 H)	4.00–4.50 (m, 8 H)	3240	–	Nujol	390 (3, M^+) 372 (4, $M^+ - H_2O$) 354 (100, $M^+ - 2H_2O$)
IIIb	0.61 (t, 6 H)	2.13 (dd, 2 H) (14.5 and 2) 2.51 (dd, 2 H) (14.5 and 10)	4.03 (m, 2 H) 4.10 (m, 4 H) 4.41 (m, 2 H)	3380 3260	– –	$CHCl_3$	418 (8, M^+) 400 (17, $M^+ - H_2O$) 383 (58) 382 (100, $M^+ - 2H_2O$)
IIIc	0.65 (t, 6 H)	2.13 (dd, 2 H) (14 and 2) 2.50 (dd, 2 H) (14 and 10.5)	4.02 (m, 2 H) 4.21 (m, 4 H) 4.41 (m, 2 H)	3280	–	Nujol	446 (8, M^+) 428 (21, $M^+ - H_2O$) 410 (100)

TABLE 3 (continued)

Compound	NMR δ (ppm)			IR ν [cm^{-1}]			Mass spectra m/e (rel.int., assignment)
	CH_3	Bridge CH_2 (J(Hz))	Ferrocene	O–H	C=O	Solvent	
IIId	0.65 (d, 12 H)	2.17 (dd, 2 H) (14 and 2) 2.58 (dd, 2 H) (14 and 10)	4.04 (m, 2 H) 4.18 (m, 4 H) 4.42 (m, 2 H)	3460 3280	–	Nujol	446 (88, M^+) 428 (15, $M^+ - H_2O$) 410 (22) 385 (100)
IIIe	0.70 (s, 18 H)	2.35 (m, 4 H)	4.08 (m, 4 H) 4.15 (m, 2 H) 4.36 (m, 2 H)	3436	–	KBr	474 (31, M^+) 400 (38) 399 (100)
IIIg	0.70 (t, 6 H) 1.02 (d, 6 H)	1.75–2.00 (m, 4 H)	3.87 (m, 2 H) 4.12 (m, 4 H) 4.29 (m, 2 H)	3250	–	HCB	398 (7, M^+) 380 (13, $M^+ - H_2O$) 362 (100)
IIIh	–	2.25 (m, 4 H)	3.94 (m, 2 H) 4.12 (m, 4 H) 4.37 (m, 2 H)	3280	–	Nujol	442 (12, M^+) 424 (99, $M^+ - H_2O$) 406 (100)

Deuterium labelled compound V

To a mixture of dry dioxane (10 ml) and D_2O (1 ml) was added 0.1 g of potasium. When the evolution of the H_2 ceased, compound Ib (0.4 g, 1 mmol) was added. The solution was heated to reflux under nitrogen for 24 h and then added to ice and water. The product was extracted with ether and the solution was dried ($MgSO_4$) and the solvent was evaporated. The residue was crystallized from n-hexane/THF (3/2). M.p. 195–197°C. Mass spectrum: ($C_{23}H_{22}D_2FeO_2$) *m/e*: 391 (3), 390 (14, M^+), 389 (12), 374 (4), 373 (27), 372 (100, $M^+ - H_2O$), 371 (82).

Complex of twist 1-methyl-1-hydroxy-3-phenyl[5]ferrocenophan-1-one with tetrahydrofurane (VI)

Compound IIa was recrystallized from n-hexane/THF (2/1). Dark-red grainy crystals were obtained. M.p. 151–152°C. IR (KBr) 3450 (s, O–H), 3320 (m, O–H), 1651 (vs, C=O) cm^{-1}; NMR ($CDCl_3$): δ 1.28 (s, 3H, CH_3), 1.84 (m, 4H, THF), 2.29 (d, 2H, *J* 6.5 Hz, bridge CH_2 adjacent to OH), 2.66 (s, 1H, OH), 2.94 (d, 2H, *J* 7.5 Hz, bridge CH_2 adjacent to C=O), 3.73 (m, 4H,THF), 4.21 (m, 3H, Fc), 4.56 (m, 2H, Fc), 4.70 (m, 2H, Fc), 4.93 (m,1H, Fc), 7.33 (m, 5H, Ph) ppm. Found: C, 70.20; H, 6.82. $C_{26}H_{30}FeO_3$ calcd.: C, 69.96; H, 6.77%.

1-t-Butyl-3-phenyl[5]ferrocenophan-1-ol (VII)

To a cooled (−5°C), stirred solution of Ie (1.1 g, 2.6 mmol) and $LiAlH_4$ (1.14 g, 30 mmol) in ether (100 ml), $AlCl_3$ (4.0 g, 30 mmol) was added in small portions. The mixture was heated to reflux for 7 h and then added to ice and water. The organic layer was separated, washed twice with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave an orange-yellow oil, which was chromatographed on silica gel with n-hexane/THF as eluent. Only one fraction was obtained. The crude product was crystallized from methanol to give 0.69 g (65%) of VII. M.p. 100–102°C; IR (HCB): 3610 (s, O–H), 1368 and 1396 (s, t-Bu) cm^{-1}; NMR (CCl_4): δ 0.70 (s, 9H, t-Bu), 1.80–2.60 (m, 6H, bridge CH_2 groups, 3.95–4.40 (m, 9H, Fc and benzylic H), 7.10–7.50 (m, 5H, Ph); mass spectrum: *m/e* 402 (73, M^+), 400 (7), 386 (23), 384 (9), 346 (30), 345 (100), 241 (84). Found: C, 74.38; H, 7.82. $C_{25}H_{30}FeO$ calcd.: C, 74.64; H, 7.51%.

Acknowledgement

We thank the Polish Academy of Science for financial support.

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