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Ferrocene compounds XXIII. [1] Synthesis and reactions of the new type of methyl ferrocyloxyalkanoates

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Abstract

The new types of ferrocenyloxaaliphatic acid ester, FcCHROCHR'COOMe (R = H, Me, Ph; R' = H, Me) (**7**) have been prepared by the action of alkoxides derived from methyl glycolate or methyl lactate on the corresponding ferrocenylcarbinyl acetates (**2**) or *N,N,N*-trimethylferrocylammonium iodides (**4**). The esters obtained were accompanied by a small quantity of oligomeric esters, $FcCHR(OCHR'CO)_nOMe$ (**9**), and with more or less ferrocyl methyl ethers (**8**). As opposed to the alkaline hydrolysis of the analogous methyl benzoxyacetate (**6**) into benzoxyacetic acid (**5**) the acidification of sodium alkanoates **10** obtained by saponification of esters **7** gave unexpectedly the corresponding ferrocenylcarbinols **1**. In a similar way the esters **7** were converted into mixtures of the mentioned carbinols and diferrocyl ethers **11** under action of aqueous hydrochloric acid. The mechanisms of the reactions **10** → **1** and **7** → **1, 11** are discussed.

Keywords: Iron; Ferrocene; Methyl ferrocyloxyalkanoates

1. Introduction

In our previous paper [1] we have described the synthesis and reactions of some ferrocylthioaliphatic acids (ferrocyl = ferrocenylmethyl). In general, such compounds can be prepared by condensation of ferrocenylcarbinols with appropriate mercaptoaliphatic acids in a strongly acidic medium. It is known from the literature that ferrocylthioaliphatic acids are useful intermediates for the preparation of optically active ferrocenylcarbinols and α-ferrocenylalkylamines [2,3], and some interesting amides *N*-substituted with penicillanic and cephalosporanic acids [4]. We have found that, contrary to benzylthioaliphatic acids, a number of ferrocylthioaliphatic acids cleaved by the action of trifluoroacetic anhydride giving 1,2-disubstituted 1,2-diferrocenylethanes and the corresponding trimeric and oligomeric species owing to the extraordinary stability of ferrocyl carbocations [1].

In continuation of our investigations of ferrocenyl-heteroaliphatic acids we decided to prepare some ferrocyloxyaliphatic acids and to investigate their reactivities and compare them with those of ferrocylthioaliphatic acids.

To our knowledge ferrocyloxyaliphatic acids, $FcCHRO(CH_2)_nCOOH$, and their derivatives have not been described in the chemical literature so far. Only a few ferrocenyloxyaliphatic acids, $FcO(CH_2)_nCOOH$, are known. Thus, for instance, ferrocenyloxyacetic acid is described as a condensation product of ferrocenyl alcohol with chloroacetic acid in an aqueous solution of potassium hydroxide [5].

Several substituted benzoxyacetic acids have been prepared in a similar way starting from benzyl alcohol and its derivatives. These compounds are stable in an acidic medium, and can be converted into the usual derivatives (salts, esters, amides, cyanides and intramolecularly cyclized products) [6–8].

2. Results and discussion

In order to obtain the model substances for our investigations, we have prepared benzoxyacetic acid (**5**)

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[1] For Part XXII, see Ref. [1].

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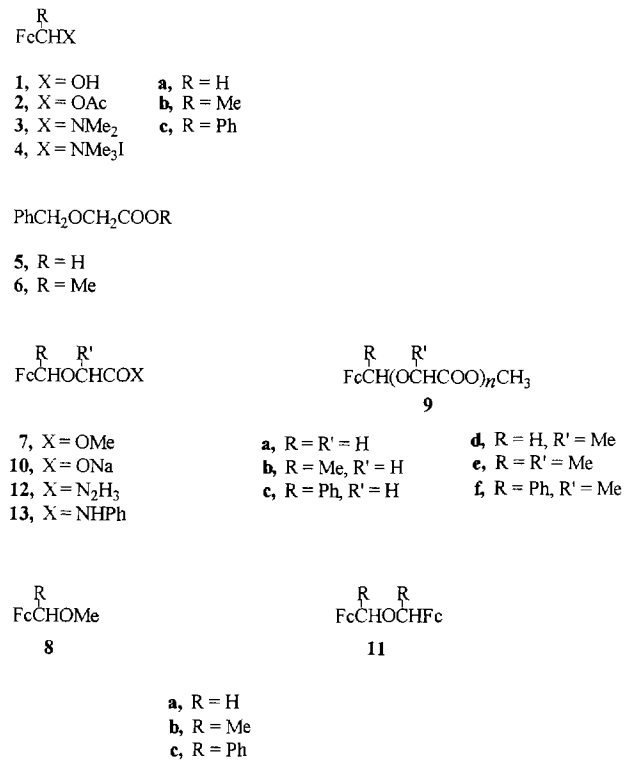


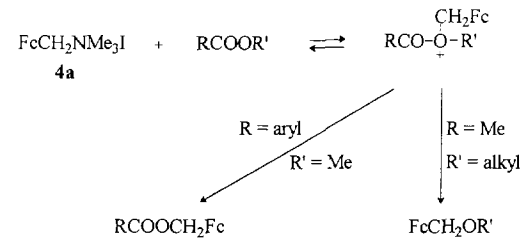
Scheme 1.

in 92% yield by the action of sodium benzoxide on chloroacetic acid in boiling toluene during 24 h. Starting from methyl chloroacetate, 67% of methyl benzoxyacetate (**6**) has been prepared in a similar manner (modification of procedures described in Refs. [6,7]). Ester **6** can be saponified into acid **5**, and the acid obtained can be reconverted into ester **6** by means of ethereal diazomethane.

Attempts to prepare the ferrocene analogues — ferrocyloxyacetic acid and methyl ferrocyloxyacetate **7a** — in a similar way were unsuccessful. Refluxing of sodium ferrocyloxide and either chloroacetic acid or methyl chloroacetate (methyl bromoacetate) for 1–2 h left the starting material unchanged or resulted in the decomposition of ferrocene compounds (Scheme 1).

It is known that ferrocyl ethers can be prepared either by starting from *N,N,N*-trimethylferrocylammonium iodide (**4a**) and the corresponding alkoxides [9], or from ferrocenylcarbinol (**1a**) and the appropriate alcohols in acetic acid [10]. One has to keep in mind that the AC1-conversions of quaternary salts **4a** with alkyl acetates gave alkyl ferrocyl ethers. In contrast, reactions of the ammonium salt **4a** and methyl arenecarboxylates gave the transesterification products [11]. It can be assumed that the conversions mentioned take place via the mechanism presented in Scheme 2.

We have planned the syntheses of the target compounds **7** on the basis of these methods by *O*-ferrocylation of the alkoxides derived from methyl hydroxyalkanoates by means of either ferrocenylcarbinyl acetates **2** or quaternary salts **4**. The analogous reactions are not described in the chemistry of benzoxyaliphatic acids. We attempted to prepare esters **7** by modifying the procedure for the related malonic ester synthesis [12]: the corresponding alkoxide was prepared from a suspension of 3 mmol of sodium in xylene and 5 mmol of methyl glycolate and refluxed subsequently with 1 mmol of salt **4a**. Very low yields of methyl ferrocyloxyacetate **7a** were obtained in these experiments. Better results were achieved using the following procedure: 3 mmol of sodium and 1 mmol of reagents **2** or **4** were added to a great excess of methyl glycolate or lactate, and the reaction mixture was refluxed for 1–3 h. The products obtained consisted of desired ferrocyloxyaliphatic acid esters **7** accompanied by a small quantity of the corresponding oligomeric esters $FcCHR(OCHR'CO)_nOMe$ (**9**) and with some ferrocyl methyl ethers (**8**). These compounds were separated by preparative thin-layer chromatography, which sometimes had to be repeated several times because of their similar R_f values. Consequently, the yields on the

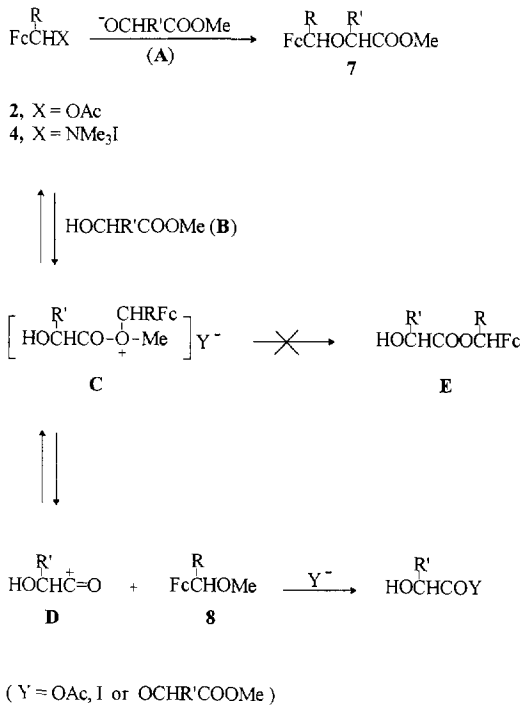


Scheme 2.

Table 1
Preparation of FcCHOCHCOOMe (**7**), FcCHOCH3 (**8**) and FcCH(OCHCOO)nMe (**9**)

Reactants			Products [a]		
FcCHX (**2**, **4**)		NaOCHCOOMe	**7**	**8**	**9**
R	X	R'	letter, yield from NMR (TLC) (%)		
H	OAc	H	**a**, 25 (20)	**a**, 75 (49)	**a**, —
H	NMe_3I	H	**a**, 60 (31)	**a**, 30 (15)	**a**, 10
Me	OAc	H	**b**, 25 (19)	**b**, 75 (50)	**b**, —
Me	NMe_3I	H	**b**, 37 (23)	**b**, 57 (25)	**b**, 6
Ph	OAc	H	**c**, 22 (18)	**c**, 73 (45)	**c**, 5
Ph	NMe_3I	H	**c**, 25 (12)	**c**, 75 (34)	**c**, —
H	OAc	Me	**d**, 30 (20)	**a**, 70 (50)	**d**, —
H	NMe_3I	Me	**d**, 65 (30)	**a**, 30 (17)	**d**, 5
Me	OAc	Me	**e**, 30 (21)	**b**, 60 (44)	**e**, 10
Me	NMe_3I	Me	**e**, 40 (26)	**b**, 60 (24)	**e**, —
Ph	OAc	Me	**f**, 25 (23)	**c**, 75 (44)	**f**, —
Ph	NMe_3I	Me	**f**, 20 (15)	**c**, 80 (49)	**f**, —

[a] Composition of the products is established from the ratio of methoxy protons' ^1H NMR signals corresponding to esters **7**, ethers **8** and oligomers **9**. In brackets are given their yields after separation by preparative TLC.



Scheme 3.

compounds obtained were relatively poor and it turned out to be impossible to prepare analytically pure samples of these oily or resinous compounds. To prove the structure of esters **7** we have prepared the corresponding hydrazides **12** and anilides **13** as homogeneous crystalline materials showing the expected results of combustion analysis. The structure of ethers **8** was additionally confirmed by comparison with the authentic samples synthesized from carbinols **1** and methanol [10]. We were able to compute the compositions of the mixtures obtained from the ratio of ^{1}H NMR signals of the methoxy protons corresponding to esters **7**, ethers **8** and oligomers **9**, which are presented in Table 1.

It can be also seen, from the same table, that the structure of the hydroxyester applied has no influence on the ratio of the esters **7** and ethers **8** obtained in these conversions. Furthermore, one can note that the reactions of quaternary salts in the sequence **4a**, **4b** and **4c** resulted in the gradual increase of ether and decrease of ester content in the products. Thus, by the action of **4a** on methyl glycolate/alkoxide 31% of ester **7a** and 15% of ether **8a** were isolated, whereas conversion of the same ester/alkoxide with **4c** gave 12% of ester **7c** and 34% of ether **8c**. As opposed to ammonium salts, acetates **2a–2e** reacted with hydroxyesters/alkoxides giving 18–23% of esters **7** and 44–50% of ethers **8**.

These results are in accordance with the above-described reactions of salt **4a** with alkoxides [9] and alkyl acetates respectively [11] (see Scheme 2), and one can propose the mechanism presented in Scheme 3 for the conversions examined.

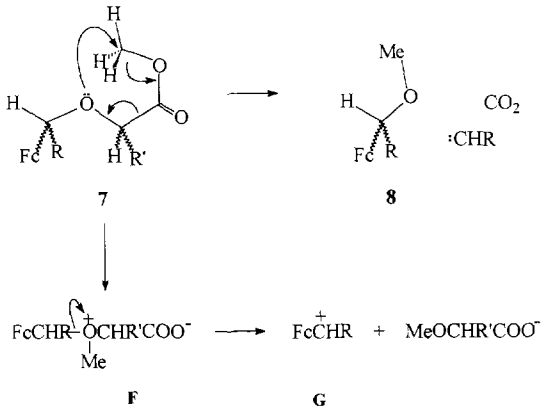
Owing to the good leaving groups (acetate, trimethylamine) the nucleophiles **A** or/and **B** substituted compounds **2** or **4** competitively. The desired ester **7** is formed by attack of the alkoxide oxygen of **A**. The oxonium species **C** is formed in the first step of the competitive reaction with **B** and then cleaved to give the acylium ion **D** and ferrocyl methyl ether **8** (AC1 mechanism). The appearance of ether **E** (formed by an alternative cleavage of oxonium **C**) was not noticed in these reactions.

It is well known that solvolysis reactions of ferrocyl acetates (and other reactions of these esters with nucleophiles) proceeded via an S_N1 mechanism with the initial heterolytic dissociation into ferrocyl cations [13]. One can anticipate a similar unimolecular mechanism in the conversions of acetates **2** with hydroxyesters where

Table 2
IR and ^{1}H NMR spectral data for $FcCHRNMe_2$ (**3**) and $FcCHRNMe_3I$ (**4**)

Compound	R	IR spectra (cm^{-1})			^{1}H NMR spectra (δ ppm)				
		ν(C–H) arom.	ν(C–H) aliph.	Ferrocene	Ferrocene protons	CH	CH_2	R	NMe_2
3a	H	3085 m	2940 m	1101 m	4.02	—	3.22	—	2.08
			2815 m [a]	1000 m	(9, m)		(2, s)		(6, s)
			2775 s [a]						
3b	Me	3090 m	2930 s	1103 m	4.00	3.53	—	1.37	2.00
			2820 s [a]	998 m	(9, m)	(1, q)		(3, d)	(6, s)
			2780 s [a]						
3c	Ph	3099 m	2950 s	1107 m	3.71	4.19	—	7.38 t, 3.25 m	2.05
		3064 w	2813 s [a]	1003 m	(s, 5H)	(m, 5H)	—	(5)	(6, s)
		3027 w	2768 s [a]						
4a	H	3060 w	2970 w	1100 m					
			2930 w	1002 m					
4b	Me	3090 w	2930 m	1103 m					
				997 m					
4c	Ph	3090 w	2970 m	1105 m					
		3020 w	2920 m	1005 m					

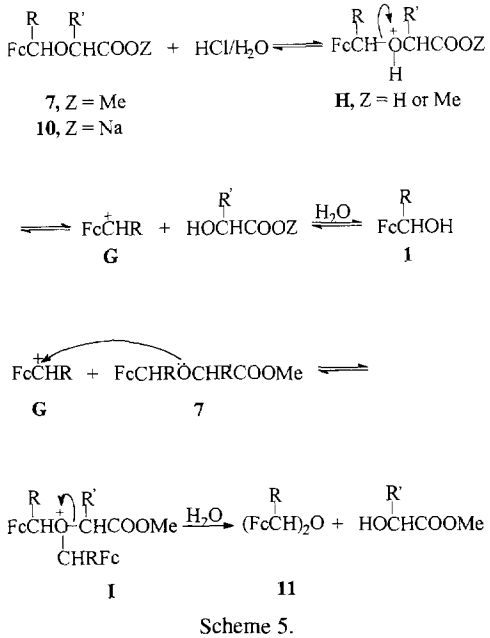
[a] The given frequencies correspond to ν_s(C–H) of the dimethylamino group.



Scheme 4.

the intermediately formed $Fc\overset{+}{C}HR$ reacts predominantly with the methoxy oxygen of **B** giving ethers **8** which are probably the products of equilibrium control. At this point one should mention that the reactions of $FcCH_2CH_2X$ (X = AcO, Br) with methyl glycolate or lactate, under the conditions described above, gave exclusively the transesterification product analogous to **E**, as the result of AL2 conversion of oxonium similar to **C** (which has to be formed by a bimolecular process) [14]. This fact and the exclusive formation of alkyl ferrocyl ethers presented in Scheme 2 supports the assumption of greater thermodynamic stability of ethers **8** in comparison to **7** and **E**.

Having in mind that the acetate is a better leaving group than trimethylamine, and on the basis of composition of products resulting from reactions of salt **4a**, one can in this case suggest a bimolecular kinetically controlled process in which esters **7a** and **7d** are formed preponderately as a consequence of attack of the more



Scheme 5.

powerful nucleophile **A**. While the conversions of **4b** yielded a little more ether than ester, ether is the main reaction product when starting from **4c**. Keeping in mind the stability sequence of the corresponding ferrocyl carbocations, $Fc\overset{+}{C}H_2 < Fc\overset{+}{C}HMe < Fc\overset{+}{C}HPh$, following the conversions **4a**, **4b**, **4c** one can assume a gradual change from a bimolecular to a unimolecular mechanism and consequently a gradual increase of ether content in the products.

Another simpler mechanism could be proposed for conversions **2(4)** → **7,8** (Scheme 4). This route involves the exclusive attack of alkoxide **A** on substrates giving esters **7** in the first step (Scheme 3). Owing to

Table 3

IR spectral data for $FcCHOCHCOOCH_3$ (**7**), $FcCHOCH_3$ (**8**) and $(FcCH)_2O$ (**11**)

Compound	R	R′	IR spectra (cm^{-1})			
			ν(CH) arom.	ν(CH) aliph.	ν(C=O)	ν(C–O)
7a	H	H	3090 m	2950 s 2920 s 2850 m	1740 s	1200 s
7b	Me	H	3095 m	2960 s 2930 s 2860 m	1740 s	1220 s
7c	Ph	H	3090 m	2950 m 2910 m 2850 w	1750 s	1210 s
7d	H	Me	3080 m	2920 s 2840 w	1740 s	1180 m 1220 s
7e	Me	Me	3090 m	2970 s 2930 s 2860 m	1735 s	1200 m
7f	Ph	Me	3090 m 3060 m	2978 m 2930 w 2869 m	1740 s	1200 m
8a	H	—	3090 m	2970 m 2920 s 2860 s	—	1170 m 1150 m
8b	Me	—	3090 m	2980 s 2940 m 2870 m	—	1170 m
8c	Ph	—	3090 m	2980 m 2920 m 2860 m	—	1190 s
11a	H	—	3100 w	2960 m 2920 m 2860 w	—	1235 s
11b	Me	—	3090 m	2970 m 2930 m 2860 w	—	1230 s
11c	Ph	—	3090 m 3030 w	2975 m 2920 m 2865 m	—	1185 s

Table 4

^{1}H NMR spectral data (δ ppm) for $FcCH_aOCH_bCOOMe$ (7)

Compound	R	R′	Ferrocene protons		Aliphatic protons						OCH_3	C_6H_5
			Subst. ring	Unsubst. ring	*a*			*b*				
					CH	CH_2	CH_3	CH	CH_2	CH_3		
7a	H	H	4.16 m	4.14 s	—	4.42	—	—	4.06	—	3.73	—
			(9)			(2, s)			(2, s)		(3, s)	
7b	Me	H	4.18 m	4.13 s	4.44	—	1.60	—	4.01	—	3.69	—
			(9)		(1, m)		(3, d)		(2, s)		(3, s)	
7c	Ph	H	4.20 m	4.14 s	5.35	—	—	—	3.97	—	3.74	7.38
			(9)		(1, s)				(2, s)		(3, s)	(5, m)
7d	H	Me	4.15m	4.13 s	—	4.26	—	4.04	—	1.36	3.73	—
			(9)			(2, m)		(1, q)		(3, d)	(3, s)	
7e	Me	Me	4.15m	4.13 s	4.39	—	1.58	4.05	—	1.37	3.75	—
			(9)		(1, m)		(3, d)	(1,q)		(3, d)	(3, s)	
7f	Ph	Me	4.24m	4.15 s	5.20	—	—	4.04	—	1.31	3.77	7.41
			(9)		(1, s)			(1, m)		(3, d)	(3, s)	(5, m)

their geometry one can imagine the formation of a five-membered transition state enabling a concerted conversion to ethers **8** followed by carbon dioxide and carbenes :CHR. Alternatively, the oxonium-carboxylate **F** could be formed as a precursor of ferrocyl cations **G** in an intramolecular S_N2 process. These carbonations could then be converted into ethers **8** in a way presented in Scheme 3. The disadvantage of the mechanism described is that it does not explain the different reactivities of acetates **2** and salts **4**.

In the next part of our investigations we have saponified esters **7** to obtain the corresponding acids. However, as distinct from the above described conversions of the analogous benzenoid ester **6** into acid **5**, the acidification of the obtained carboxylates **(10)** resulted in their cleavage into starting carbinols **1**.

The key intermediates in these conversions are probably the oxonium species **H** which cleaves into ferrocyl cations **G** owing to their extraordinary stability. These carbocations yield carbinols **1** in an aqueous medium. It should be mentioned that alkaline solutions of carboxylates **10** are very stable and did not change by standing for several months (Scheme 5).

We have found that the action of aqueous hydrochloric acid (1:1) on esters **7** at pH ~ 5 resulted in their partial cleavage into carbinols. In contrast to the instantaneous quantitative cleavage **10** → **1**, the conversions of esters **7** with aqueous hydrochloric acid at pH ~ 1 at room temperature gave mixtures of carbinols **1** and diferrocyl ethers **11** during a period of 8–24 h (after 1–3 h carbinols predominated in the mixtures obtained). On the other hand we have noticed that even prolonged

Table 5

^{1}H NMR spectral data (δ ppm) for $FcCHOCH_3$ (8) and $(FcCH)_2O$ (11)

Compound	R	Ferrocene protons		Aliphatic protons			OCH_3	C_6H_5
		Subst. ring	Unsubst. ring	CH	CH_2	CH_3		
8a	H		4.13 m	—	4.23 m	—	3.31	—
			(11)				(3, s)	
8b	Me		4.13 m	4.21 m	—	1.53	3.25	—
			(10)			(3, d)	(3, s)	
8c	Ph	4.25(1, m)	4.09	—	5.00	—	3.29	7.40
		4.07(2, m)	(5, s)		(1, s)		(3,s)	(5,m)
		3.94(1,m)						
11a	H	4.14 t	4.11 s	—	4.29	—	—	—
		4.23 t			(4,s)			
			(18)					
11b	Me	4.15 m	4.09 s	4.40	—	1.43 d	—	—
		4.22 m		(2,m)		1.49 d		
			(18)				(6) [a]	
11c	Ph	3.89 m	4.10 s	4.99	—	—	—	7.35
			(18)	(2,s)				(10,m)

[a] From the ratio of the signals corresponding to the given doublets one can see the compound **11b** consisted of aproximately equal parts of racemate and *meso* forms.

Table 6

Physical constants and IR spectral data for $FcCHOCHCONHNH_2$ (12)

Compound	R	R′	Formula (M_r)	Yield (%)	Analysis, found (calcd.) (%)			IR spectra (cm^{-1})			
					C	H	N	ν(CH) arom. (aliph.)	ν(NH)	ν(C=O)	δ(NH)
12a	H	H	$C_{13}H_{16}FeN_2O_2$ (288.1)	30	54.40 (54.16)	5.82 (5.60)	9.61 (9.72)	3080 w (2950 w, 2920 m, 2850 w)	3420 w 3300 m	1670 s	1620 m
12b	Me	H	$C_{14}H_{18}FeN_2O_2$ (302.1)	41	55.88 (55.62)	6.30 (6.01)	9.01 (9.27)	3090 m (2980 m, 2920 m, 2850 w)	3440 w 3300 m	1660 s	1615 m
12c	Ph	H	$C_{19}H_{20}FeN_2O_2$ (364.1)	25	62.34 (62.62)	5.71 (5.54)	7.91 (7.69)	3090 w 3025 w (2970 w, 2920 w, 2854 w)	3442 m 3334 w	1680 s	1626 m
12e	Me	Me	$C_{15}H_{20}FeN_2O_2$ (316.1)	31	57.12 (56.95)	6.53 (6.38)	9.01 (8.86)	3090 w (2990 m, 2935 w)	3439 m	1673 s	1624 m
12f	Ph	Me	$C_{20}H_{22}FeN_2O_2$ (378.1)	33	63.13 (63.47)	5.70 (5.86)	7.68 (7.41)	3090 w 3030 w (2977 m, 2930 m)	3440 m	1684 s	1625 m

standing of carbinols **1** in an acidic medium left only unchanged material.

In the light of the mechanism of reactions **10** → **1** and on the basis of the experimental data mentioned, for the conversions of esters **7** one can assume a similar intermediate formation of ferrocyl cations **G** which undergo either conversion into carbinols **1** or nucleophilic attack of ether oxygen of ester **7**, giving oxonium species **I** then being cleaved to give *sym*-ethers **11** (Scheme 5). The following facts are also in accordance with the proposed mechanism: conversions **7** → **11** are faster and the products are gradually enriched in *sym*-ethers in the sequence **7a**,**7d** < **7b**,**7e** < **7c**,**7f**. This finding supports the S_N1 mechanism via the corresponding carbocations, whose stability increases in the given sequence (Scheme 5).

3. Experimental details

Melting points were determined with a Buechi apparatus. The IR spectra were recorded for KBr pellets or CCl_4 solutions with a Bomem MB100 Mid FT IR spectrophotometer. The ^1H NMR spectra of $CDCl_3$ solutions were recorded on a Varian EM 360 or Varian Gemini 300 spectrometer with tetramethylsilane as internal standard. Products were purified by preparative thin layer chromatography on silica gel (Merck, Kieselgel 60 HF_{254}) using the mixtures benzene–ethanol or benzene as eluents or by recrystallization from (aqueous) ethanol. Reduction of the appropriate acylferrocenes gave ferrocenylcarbinols (**1**) [15] which were transformed into ferrocenylcarbinyl acetates (**2**) by the action of acetic anhydride in pyridine [16] or acetic acid in dry benzene [17]. *N*,*N*-Dimethylferrocylamines (**3**) (Table 2) have been prepared from ferrocene and *N*,*N*,*N*,*N*-tetramethyldiaminomethane [18] and by dimethylamination of acetate (**2b**) [17] or carbinol (**1c**) [19]. Quaternization of amines **3** with methyl iodide in acetone gave *N*,*N*,*N*-trimethylferrocylammonium iodides (**4**) (Table 2) [20]. Methyl glycolate and methyl lactate were prepared by esterification of the appropriate hydroxyaliphatic acids in methanol in the presence of Woffatit KPS [21].

3.1. Benzoxyacetic acid (5) and methyl benzoxyacetate (6)

3.57 g (33 mmol) of the freshly distilled benzyl alcohol was added to a solution of 690 mg (30 mmol) of sodium in 15 ml of ethanol abs. After heating the reaction mixture at 100 °C for 0.5 h the excess of ethanol was thoroughly evaporated under reduced pressure. The obtained sodium benzoxide was suspended in 10 ml of toluene abs. and 1.42 g (15 mmol) of chloroacetic acid dissolved in 5 ml of the same solvent was added. After refluxing for 24 h the reaction solution was extracted several times with water. The aqueous layer was acidified with hydrochloric acid and extracted with diethyl ether. The organic phase was washed with water, dried over $MgSO_4$ and evaporated to dryness to leave 2.2 g (92%) of benzoxyacetic acid (**5**) [6,7]. IR (CCl_4): ν(OH) COOH 3000 b, ν(C=O) COOH 1720 s, ν(CO) COOH 1205 s cm^{-1}.

In a similar way, as described above, 1.82 g (67%) of methyl benzoxyacetate (**6**) was obtained from 3.57 g of

Table 7
^1H NMR spectral data (δ ppm) for $Fc\overset{R}{\underset{}{C}}H_2O\overset{R'}{\underset{}{C}}H_2CONHNH_2$ (**12**)

Compound	Ferrocene protons		Aliphatic protons						Ph	NH	NH_2
	Subst. ring	Unsubst. ring	*a*			*b*					
			CH	CH_2	CH_3	CH	CH_2	CH_3			
12a	4.22 m	4.14 s (9)	—	4.35 (2, s)	—	—	4.03 (2, s)	—	—	7.75 (1, b)	3.85 (2, b)
12b	4.24 m	4.14 s (9)	4.38 (1, q)	—	1.59 (3, d)	—	3.98 (2, s)	—	—	7.57 (1, b)	3.80 (2,b)
12c	4.14 m 4.19 m	4.03 s (9)	5.18 (1, s)	—	—	—	3.97 (2, s)	—	7.39 (5, m)	7.75 (1, b)	3.85 (2, b)
12d	4.21 m	4.15 s (9)	—	4.36 (2, s)	—	4.06 (1, m)	—	1.30 (3, d)	—	7.60 (1, b)	3.80 (2, b)
12e [a]	4.21m	4.14 s (9)	4.39 (1, m)	—	1.59 d 1.56 d (3)	4.07 (1, m)	—	1.35 d 1.27 d (3)	—	7.69 b 7.49 b (1)	3.83 b 3.65 b (1)
12f [a]	4.19 m	4.01 s 4.03 s (9)	5.16 s 5.28 s (1)	—	—	3.99 (1, m)	—	1.25 d 1.45 d (3)	7.37 m 7.42 m (5)	7.75 b 7.87 b (1)	3.80 (2, b)

[a] These compounds consisted of two diastereoisomeric pairs of enantiomers. From the ratios of the well-separated doublets corresponding to *b*-methyl groups one can see the composition of these pairs is 50:50 for **12e** and 33:67 for **12f**.

Table 8
Physical constants and IR spectral data for $FeCH(R)OCH(R')CONHPh$ (**13**)

Compound	R	R′	Formula (M_r)	Yield (%)	Analysis, found (calcd.) (%)			IR spectra (cm^{-1})			
					C	H	N	ν(CH)arom. (aliph.)	νNH	ν(C=O)	δ(NH)
13a	H	H	$C_{19}H_{19}FeNO_2$ (349.2)	46	65.05 (65.32)	5.63 (5.49)	4.30 (4.01)	3085 m 3030 m (2950 w, 2900 w, 2850 w)	3450 w 3370 s	1670 s	1600 s
13b	Me	H	$C_{20}H_{21}FeNO_2$ (363.1)	45	65.92 (66.10)	5.98 (5.83)	3.52 (3.86)	3090 w 3040 m (2970 m, 2910 m, 2850 w)	3370 m	1670 s	1596 s
13c	Ph	H	$C_{25}H_{23}FeNO_2$ (425.1)	25	70.71 (70.57)	5.19 (5.45)	3.40 (3.29)	3086 w 3030 w (2967 w, 2926 w, 2869 w)	3385 m	1679 s	1600 m
13d	H	Me	$C_{20}H_{21}FeNO_2$ (363.1)	29	66.34 (66.10)	6.08 (5.83)	3.57 (3.86)	3090 m 3030 w (2980 w, 2920 w, 2860 w)	3380 m	1675 s	1595 s
13e	Me	Me	$C_{21}H_{23}FeNO_2$ (377.1)	40	67.09 (66.82)	6.34 (6.15)	4.00 (3.71)	3085 w 3030 w (2985 m, 2936 m, 2850 w)	3384 m	1682 s	1601 m
13f	Ph	Me	$C_{26}H_{25}FeNO_2$ (439.1)	49	71.29 (71.05)	5.99 (5.74)	3.32 (3.19)	3090 w 3030 w (2978 w, 2930 w)	3386 s	1680 s	1602 m

Table 9

^{1}H NMR spectral data (δ ppm) for $Fc\overset{R}{C}H_a\overset{R'}{O}CH_bCONHPh$ (**13**)

Compound	Ferrocene protons		Aliphatic protons						Ph			NH
	Subst. ring	Unsubst. ring	*a*			*b*						
			CH	CH_2	CH_3	CH	CH_2	CH_3				
13a	4.22 m	4.16 s	—	4.45	—	—	4.06	—	7.52	7.32	7.14	8.22
	4.27 m			(2, s)			(2, s)		(2, d)	(2, q)	(1, q)	(1, b)
	(9)											
13b	4.22 m	4.16 s	4.48	—	1.16	—	4.04	—	7.51	7.31	7.10	8.23
	4.27 m		(1, q)		(3, d)		(2, s)		(2, d)	(2, t)	(1, t)	(1, b)
	(9)											
13c	4.15 m	4.02 s	5.30	—	—	—	4.00	—	7.59 m	7.35 m	7.11 m	8.40
	4.20 m		(1, s)				(2, s)			(10)		(1, b)
	(9)											
13d	4.20 m	4.14 s	—	4.48	—	4.07	—	1.40	7.58	7.43 7.30	7.11	8.40
	(9)			(2, s)		(1, m)		(3, d)	(1, d)	(1, d) (2, m)	(1,m)	(1, b)
13e [a]	4.20 m	4.13 s	4.45	—	1.67 d	4.08	—	1.36 d	7.57	7.45 7.30	7.10	8.28 b
	4.26 m	4.15 s	(1, m)		1.63 d	(1, m)		1.43 d	(1, d)	(1, d) (2, m)	(1,m)	8.44 b
	(9)				(3)			(3)				(1)
13f [a]	4.22 m	4.07 s	5.23 s	—	—	3.96	—	1.31 d	7.61 m	7.40 m	7.12 m	8.42 b
	(9)		5.33 s			(1, m)		1.53 d		(10)		8.60 b
			(1)					(3)				(1)

[a] See the footnote in Table 7; the composition of the two diastereoisomeric pairs of enantiomers is 45:55 for **13e** and 50:50 for **13f**.

benzyl alcohol, 690 mg of sodium, and 1.63 g (15 mmol) of freshly distilled methyl chloroacetate after refluxing for 30 h. ^{1}H NMR ($CDCl_3$): δ 7.35 (5H, m, Ph), 4.62 (2H, s, PhCH_2), 4.10 (2H, s, CH_2CO), 3.74 (3H, s, Me). IR (CCl_4): ν(CH) Ph 3030 s, ν(CH) aliph. 2965 s, ν(C=O) COOMe 1750 s, ν(C–O) COOMe 1210 s cm^{-1}.

Ester **6** can be saponified in the usual manner giving 82% of acid **5**. Esterification of acid **5** by means of ethereal diazomethane in methanol yielded 78% of ester **6**. The IR spectra of the so obtained compounds were superimposable with the originally prepared specimens.

3.2. Methyl ferrocyloxyacetates (7a–7c), methyl 2-ferrocyloxypropionates (7d–7f), ferrocyl methyl ethers (8) and oligomers (9)

3.2.1. Procedure A

The attempts to prepare esters **7** starting from carbinols **1** and methyl chloroacetate (methyl bromoacetate), as described in Section 3.1. were unsuccessful. Refluxing for 1–2 h resulted in decomposition of ferrocene compounds.

3.2.2. Procedure B

69 mg (3 mmol) of molten sodium in dry xylene was converted into a fine dispersion by shaking and 5 mmol of the corresponding methyl hydroxyalkanoate was added. After stirring for 15 min at 110 °C sodium disappeared and 380 mg (1 mmol) of *N,N,N*-trimethylferrocylammonium iodide (**4**) was added. After reflux for 3 h, the reaction mixture was poured into ice–water, extracted with diethyl ether, washed with saturated aqueous solution of sodium chloride, dried over magnesium sulphate and evaporated to dryness, giving resinous product consisting of 7% of **7** and 5% of **8**.

3.2.3. Procedure C

690 mg (30 mmol) of sodium was added with mechanical stirring to ca. 8 ml of methyl glycolate or methyl lactate. After formation of the corresponding sodium alkoxides 10 mmol of acetates **2** or quaternary salts **4** was added and the reaction solution refluxed for 2–5 h. The mixture was cooled to room temperature, poured into a double volume of water and extracted with diethyl ether. The ethereal layer was thoroughly washed with water to eliminate the residual methyl hydroxyalkanoate and sodium hydroxide, dried over $MgSO_4$ and evaporated to dryness to leave yellow brownish resinous products (Tables 1, 3 and 4).

3.3. Saponification of methyl ferrocyloxyalkanoates (7) and decomposition of sodium ferrocyloxyalkanoates (10)

A solution of 50 mmol of esters **7** in 10 ml of methanol containing 40 mg (80 mmol) of sodium hydroxide and two drops of water was refluxed for 2–3 h. Methanol was evaporated, residuum diluted with water and washed with diethyl ether leaving alkaline solution of salts **10**, which were acidified with aqueous hydrochloric acid (1:1) to pH ~ 1 and extracted with ether giving 35% of carbinols **1**. The physical properties of the alcohols

obtained were identical with the originally prepared ones [15].

3.4. Decomposition of methyl ferrocylalkanoates (7) into ferrocenylcarbinols (1) and diferrocyl ethers (11)

0.1 mmol of esters **7** was dissolved in 5 ml of diethyl ether and 3 ml of aqueous hydrochloric acid (1:1) was added. The reaction mixture was vigorously stirred at room temperature for 24 h, and its composition was examined every 30 min by means of TLC. Mixtures of carbinols **1** and *sym*-ethers **11** have been obtained (Tables 3 and 5).

3.5. Hydrazides of ferrocyloxyacetic acid and 2-ferrocyloxypropionic acid (12)

A mixture of 1 mmol of esters **7** and 1 ml of hydrazine hydrate was gently heated under reflux for 15 min. Then just enough ethanol abs. (ca. 6 ml) was added through the condenser to produce a clear solution. The reaction mixture was refluxed for a further 2–3 h and ethanol was evaporated. The resinous raw product was dissolved in dichloromethane, washed with water several times, dried over $MgSO_4$ and evaporated to dryness (Tables 6 and 7).

3.6. Ferrocyloxyacetanilides and 2-ferrocyloxypropionanilides (13)

61.5 mg (0.66 mmol) of fresh distilled aniline was added to a cold solution of ethylmagnesium bromide prepared from 14.6 mg (0.6 mmol) of magnesium, 218 mg (2 mmol) of ethyl bromide and 5 ml of sodium-dried diethyl ether. After the vigorous evolution of ethane had ceased, 0.3 mmol of esters **7** in 3 ml of diethyl ether was added, and the mixture refluxed for 10 min. After cooling the reaction mixture was diluted with ether and acidified with aqueous hydrochloric acid. The organic layer was washed with water, dried with $MgSO_4$ and evaporated to dryness (Tables 8 and 9).

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