CROATICA CHEMICA ACTA CCACAA **70** (4) 1021–1037 (1997)

ISSN–0011-1643
CCA–2472

Original Scientific Paper

Ferrocene Compounds. XXIV. Synthesis and Reactions of Some ω,ω'-(1,1'-Ferrocenylene)bis(thiaaliphatic Acids)

Srđan Lisac, Vladimir Rapić, Zoran Zorić, and Nevenka Filipović-Marinić*

Faculty of Food Technology and Biotechnology, University of Zagreb, 10000 Zagreb, Croatia

Received November 5, 1996; revised March 10, 1997; accepted March 20, 1997

Condensations of several α,α'-disubstituted 1,1'-ferrocenylenebis-carbinols (**1**) with mercaptoethanoic acid, 3-mercaptopropanoic acid or 3-acetylthio-2-methylpropanoic acid in the presence of trifluoroacetic acid have given the corresponding 1,1'-ferrocenylene-bisthiaaliphatic acids (**2–4**) in 49–90% yields. Reactions of acids **2–4** with trifluoroacetic anhydride yielded 15–29% of *trans*-2-oxa[3]ferrocenophanes (*trans*-**8**), 7–13% of [2,2]ferrocenophanes (**9**) and 8–15% of the ethanoferrocenylene oligomers (**10**). The mechanism of the reactions is discussed.

INTRODUCTION

In previous papers[1,2] we have described the synthesis and reactions of some ferrocenylheteroaliphatic acids. Ferrocylthioaliphatic acids[#,1] have been prepared by condensation of α-substituted ferrocenylcarbinols with mercaptoethanoic acid, 3-mercaptopropaonic acid or 3-mercapto-2-methylpropanoic acid in the presence of trifluoroacetic acid (TFA). We have found that, instead of the expected intramolecularly cyclized products, reactions of the acids obtained with trifluoroacetic anhydride (TFAA) gave 23–30% of the 1,2-disubstituted 1,2-diferrocenylethanes, 15–26% of the corresponding trimers ($FcCHRCHR(FnCHR)_nFc$, $n = 1$)[##] and about 30% of oligomeric spe-

* Author to whom correspondence should be addressed.
[#] Ferrocyl = ferrocenylmethyl.
[##] Fc = ferrocenyl, Fn = 1,1'-ferrocenylene.

cies (n = 2, 3). We have prepared the new type of ferrocenyloxaaliphatic acid esters FcCHROCHR'COOMe[2] by the action of alkoxides derived from methyl hydroxyalkanoates on the corresponding ferrocenylcarbinyl acetates or *N,N,N*-trimethylferrocylammonium iodides. As opposed to the alkaline hydrolysis of the analogous methyl benzoxyacetate into benzoxyacetic acid, the acidification of the sodium salts [FcCHROCHR'COONa] obtained by saponification of the related esters gave the corresponding ferrocenylcarbinols. In a similar way, ferrocyloxyaliphatic esters were converted into a mixture of the mentioned carbinols and α,α'-disubstituted diferrocyl ethers upon treatment with aqueous hydrochloric acid. We assumed that the demonstrated reactions of the ferrocenylheteroaliphatic acid prepared took course *via* extraordinary stable ferrocyl carbocations.[3]

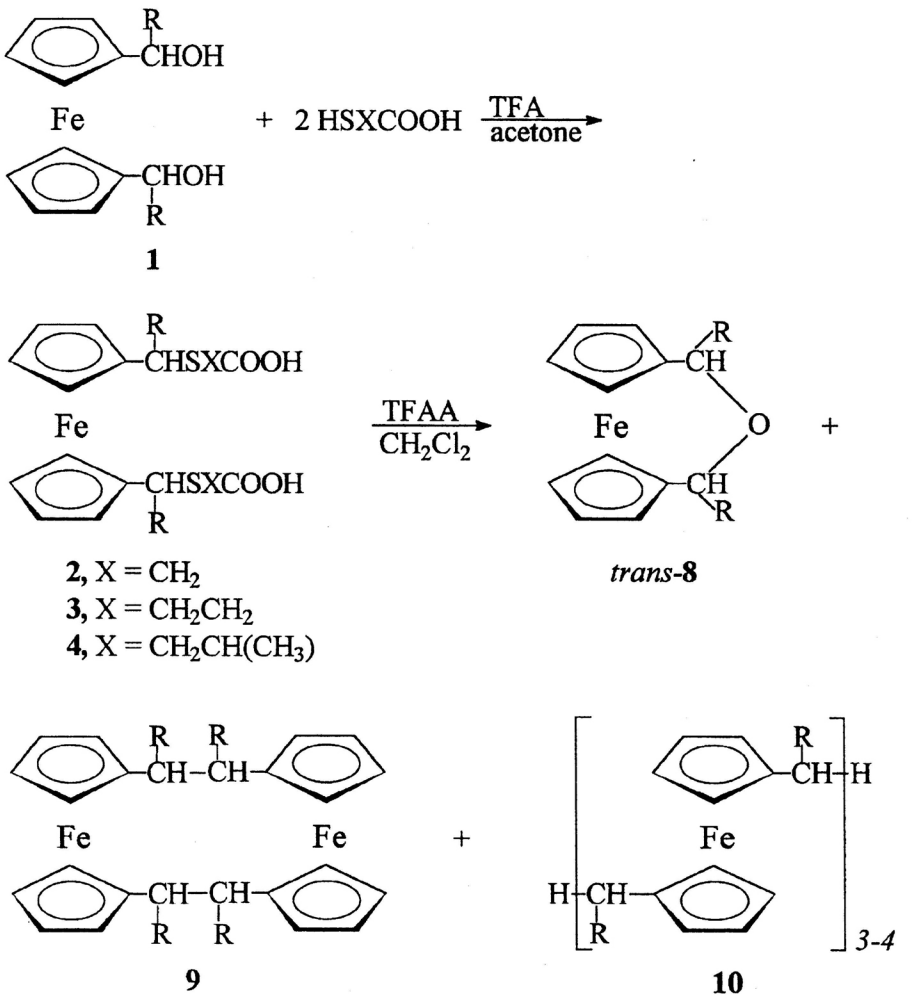
These results prompted us to extend our investigations to the 1,1'-ferrocenylenebis(heteroaliphatic acids). There are only few reports on the preparation of such compounds in the literature. Several ω,ω'-disubstituted ω,ω'-(1,1'-ferrocenylene)bis(3-thiabutanoic acids) were prepared by the reactions of the corresponding α,α'-disubstituted 1,1'-ferrocenylenebismethanols with mercaptoethanoic acid in dichloromethane in the presence of TFA.[4] These thiaacids were converted into ferrocene-containing penicillins and cephalosporins.[5]

The main objective of this work was to generate the α-ferrocenyl carbocations by the action of TFAA on the 1,1'-ferrocenylenebis(thiaaliphatic acids) in order to investigate the mode of their reactions which possibly involve the intra- and/or intermolecular combination.

RESULTS AND DISCUSION

We have prepared a range of thia analogues of 1,1'- ferrocenylenebis(aliphatic acids) using the same method as described previously:[1] condensations of biscarbinols **1** with mercaptoethanoic acid, 3-mercaptopropanoic acid or 3-acetylthio-2-methylpropanoic acid were performed in acetone by means of TFA giving 49–90% of the corresponding bis(thiaaliphatic acids) **2–4**. Most of the acids obtained are well defined crystalline compounds and were identified from their spectral data and by conversion into methyl esters **5–7**. The ^{1}H-NMR spectral data indicate that compounds **5** are mixtures of *meso* and racemic forms (in ratios 0.8–2), while esters **6** and **7** consisted of several stereomers. The configuration and stereomeric ratio of esters **5** was determined from chemical shifts and intensities of NMR signals due to the methine protons (H_c) based on the anisotropic shielding effects by methyl or phenyl group. Similar shielding effects were operative in *meso* and racemic diols **1a** and **1b**.[6]

With the specific reactions of ferrocylthioaliphatic acids, FcCHRSXCOOH, with TFAA[1] in mind, we explored the action of the same reagent on the bis-



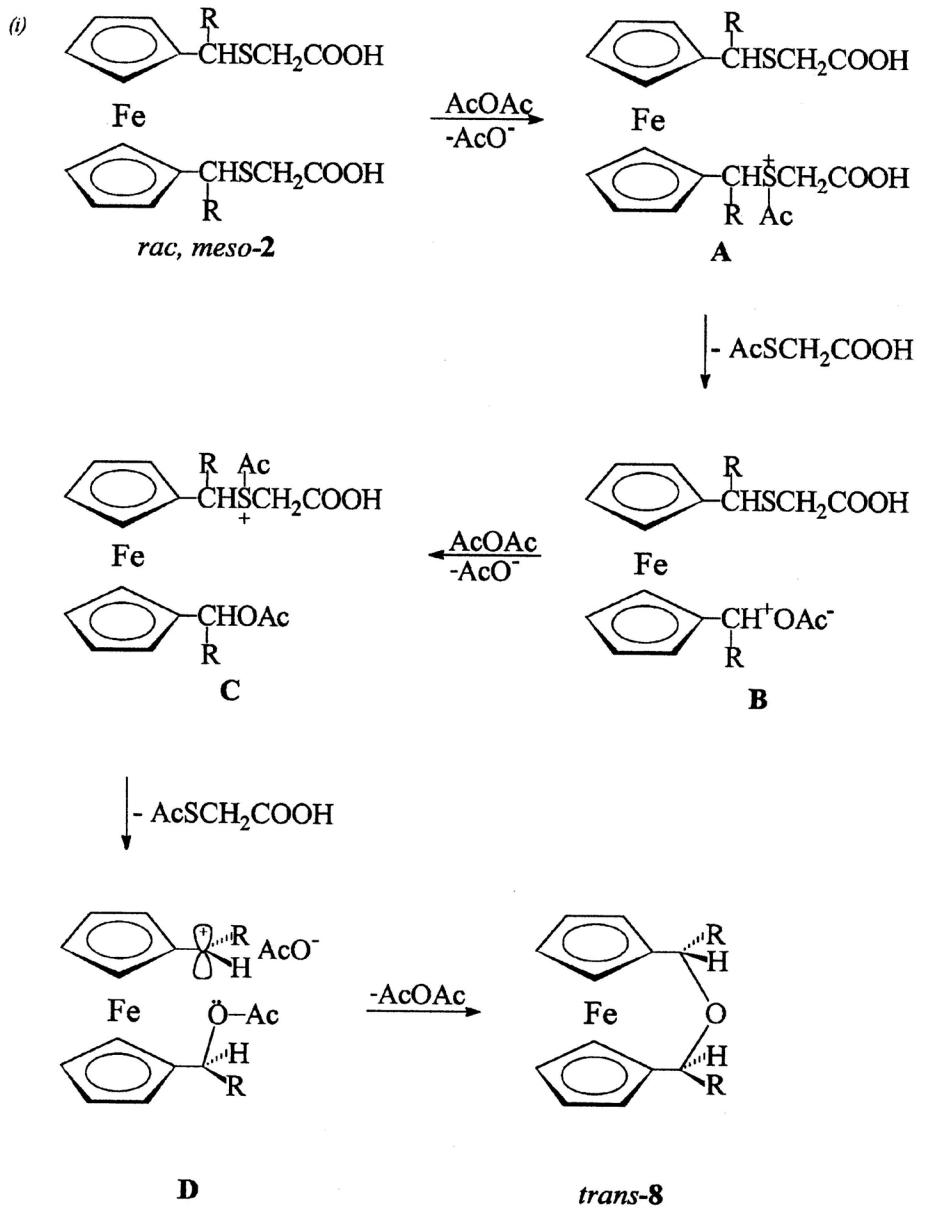
a, R = Me
b, R = Ph
c, R = *p*-ClC_6H_4
d, R = *p*-$CH_3C_6H_4$
e, R = *p*-$CH_3OC_6H_4$

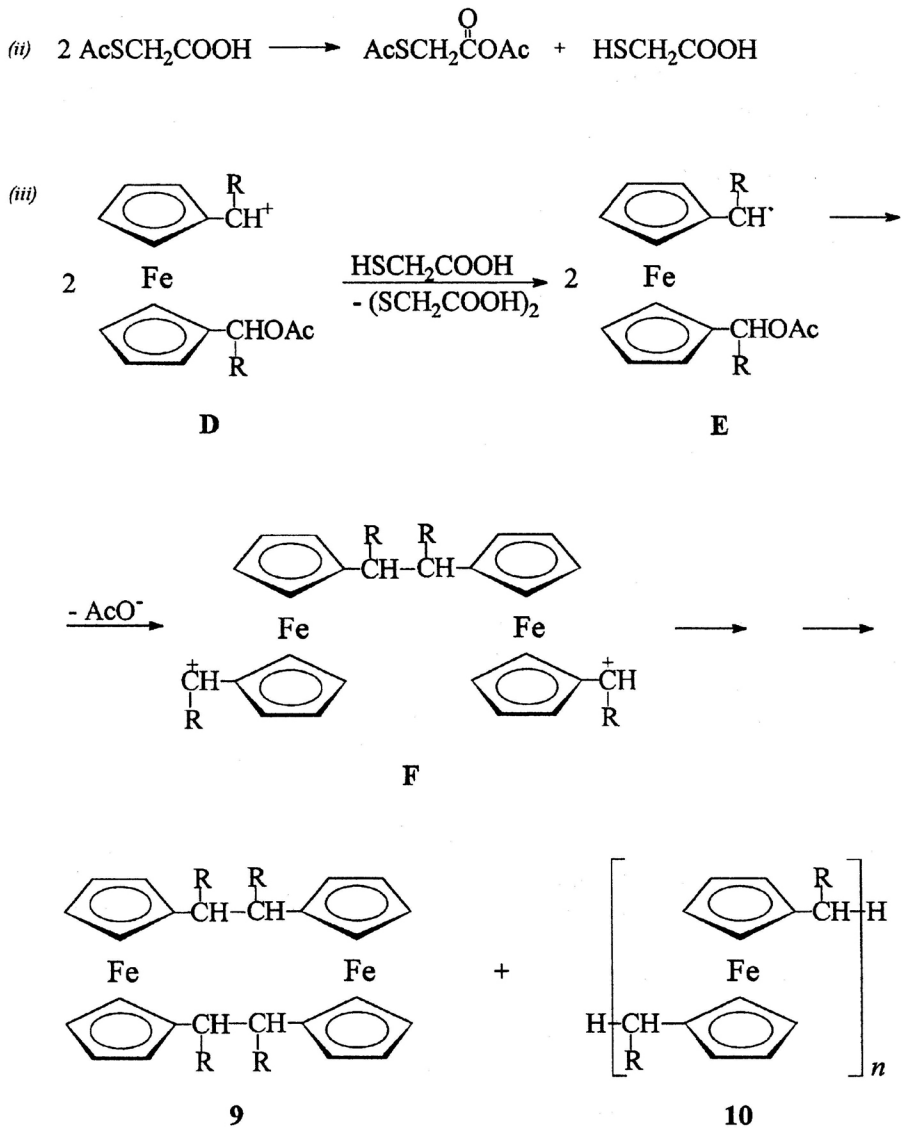
Scheme 1.

acids **2–4** in dichloromethane solutions. In reactions of ω,ω′-(1,1′-ferrocenylene)bis(3-thiaaliphatic acids) (**2**) with TFAA, we obtained 15–29% of the cyclic ethers **8** and 9–11% of [2,2]ferrocenophanes **9** along with the ex-

pected oligomeric ethanoferrocenylene species (**10**, 10–15%). The analogous reactions of acids **3** and **4** gave the same products.

In considering the possible mechanism of reactions **2** → **9**, **10** we considered the following points could be important (Scheme 2).





Scheme 2.

(*i*) Taking into account the nuchleophilic character of sulfur groups, we assumed *S*-acylation of thiaacids by means of TFAA, and the subsequent cleavage of the resultant sulfonium species **A** and **C** to fer-

rocyl carbocations **B** and **D** under formation of thioester-acid, CF_3COSCH_2COOH. Ferrocyl cations **B** and **D** are likely intermediates as it is known that 1,1′-dications are not formed under the reaction conditions (*e.g.* dicarbinols of type **1** gave in TFA only monocarbonium ions[7]). The possibility of S_N1 conversion of **D** into ferrocenophane **8** is obvious.

(ii) The disproportionation of CF_3COSCH_2COOH into $CF_3COSCH_2COOCOCF_3$ and mercaptoethanoic acid can be expected as a consequence of the strong acylating ability of thioesters.

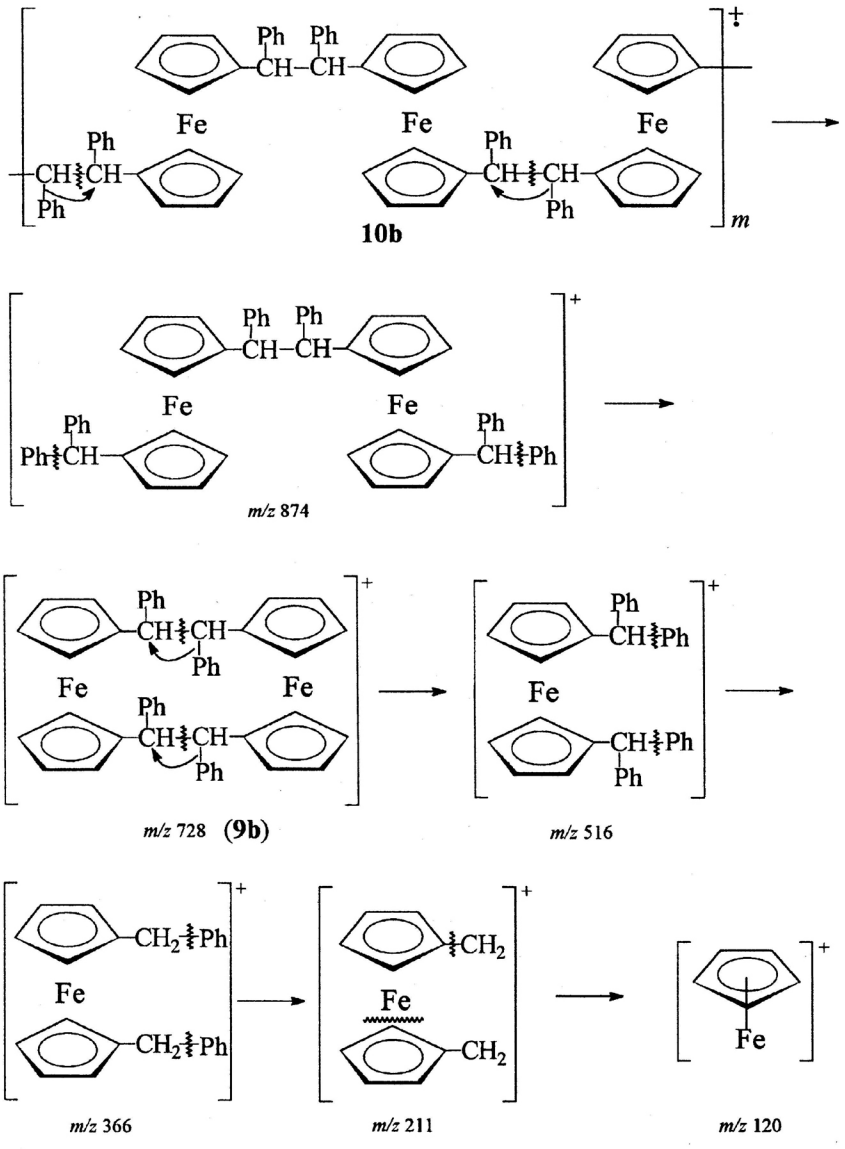
(iii) The observed reduction of ferrocyl cations by amines to radicals and their dimerization[8] suggested strongly a similar fate of cations **D**: mercaptoethanoic acid (which is a much stronger reducing agent than amines) could well cause their reduction to neutral Fe(II) radicals **E** which then dimerize with the formation of dications **F** by loss of trifluoroacetate. These intermediates are in a similar reaction sequence converted to dimers **9** and oligomers **10**.

It is noteworthly that the mechanisms proposed involve formation of the very reactive intermediate species, such as the thioester-acid and thioester-anhydride which could well account for the catalytic role of TFAA.

K. Yamakawa and M. Hisatome[6] have reported that the ring-closure of α,α′-disubstituted 1,1′-ferrocenylenebiscarbinols (**1**, R = Me, Ph) induced by treatment with diluted HCl into the corresponding 2-oxa[3]ferrocenophanes (**8**) proceeds in a stereoselective fashion: *meso*-diol gave *trans*-ether and racemic diol was converted into *cis*-ether. On the basis of the well-known fact that the solvolysis of ferrocenylcarbinol derivatives proceeds *via* a first-order reaction mechanism,[9] the authors suggested the similar S_N1 process for the desribed transformations. The stereochemistry of this reaction is interpreted by intermediate formation of the corresponding monocarbocations, which underwent a slow equilibration (the existence of such intermediates is demonstrated by identical ^{1}H-NMR spectra of cyclic ethers and of the corresponding diols recorded in TFA).

In our experiments, we started from mixtures of racemic and *meso*-1,1′-ferrocenylenebis(3-thiabutanoic acids) (**2**) (see Table IV) but we isolated only one heteroannularly cyclized sterochemical species **8**. By comparison of the ^{1}H-NMR spectra of *cis*- and *trans*-ethers **8a** and **8b** obtained by Yamakawa and Hisatome[6] with the spectra of our products (**8a–8e**), we concluded (on the basis of well separated singlets at higher field, δ = 4.99–5.15 ppm, corresponding to the methine protons shielded by the methyl group or benzene nucleus on the other cyclopentadienyl ring) that we obtained products of *trans*-configurations in all the cases. In the experiment with diluted HCl, there is nothing special to stabilize the intermediate ferrocyl cations, which are therefore highly reactive, so that little time is left for rotation around the C-C bond between the cyclopentadienyl ring and the cationic centre. On

the other hand, in our conversions **2** → **8**, excess of TFAA provides a medium that stabilizes cation **D** by solvation[10] and therefore sufficient time is left to rotate around this bond, leading finally to the thermodynamically more stable *trans*-product (see Scheme 2). On the whole, the course of the reaction is determined mainly by solvation, which affects the lifetime of the cations



Scheme 3.

and probably, to a lesser degree, by lower basicity (nuchleophilicity) of the single bonded oxygen in intermediate **D** than that of the hydroxyl oxygen of the ferrocyl cations derived from biscarbinols **1**.

[*m,m*]Ferrocenophanes (*m* = 0, 1, 3, 4) accompanied by small quantities of the corresponding oligomers are described as products of the action of ferric chloride on the disodium salts of α,ω-dicyclopentadienylalkanes.[11] [2,2]Ferrocenophanes **9** and oligomers **10** have not been decribed in chemical literature so far. From the NMR spectra we have obtained only an indication for oligomeric constitution of **10**. Their degrees of polymerization were estimated by gel permeation chromatography, indicating tri- and tetrameric structures. No molecular ions have been detected in the mass spectra of the oligomers, but the most intense fragments of ions indicated the proposed structure. The possible fragmentation pattern is presented in Scheme **3**.

EXPERIMENTAL

The melting points were determined with Buchi apparatus. The IR spectra were recorded for KBr pellets or liquid films with a Bomem MB 100 Mid FT IR spectrophotometer. The ^{1}H-NMR spectra of $CDCl_3$ solutions (if not stated otherwise) were recorded on a Varian EM 360 or Varian Gemini 300 spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained with a Shimadzu GCNS-QP 1000 spectrometer. Degrees of polymerization of oligomers were determined by gel permeation chromatography (GPC) on a 500 A PL gel column (Varian 8500 pump; tetrahydrofuran as eluent). Products were purified by preparative thin layer chromatography (TLC) on silica gel (Merck, Kieselgel 60 HF_{254}) using benzene or benzene-ethanol mixtures as eluents, or by recrystallization from (aqueous) ethanol or hexane-dichloromethane mixtures.

α,α′-Disubstituted 1,1′-ferrocenylenebismethanols (**1a–1e**) were obtained by reduction of the corresponding ketones with sodium borohydride in isopropyl alcohol.[12]

ω,ω′-Disubstituted ω,ω′-(1,1′-ferrocenylene)bis(3-thiabutanoic acids) (2), -(4-thiapentanoic acids) (3) and -(2-methyl-4-thiapentanoic acids) (4)*

Mercaptoethanoic acid, 3-mercaptopropanoic acid,** or 3-acetylthio-2-methylpropanoic acid (10 mmol) was added to a solution of the corresponding carbinol **1** (5 mmol) in 5–10 ml of acetone. To TFA (0.1 ml), the mixture was added under stirring, and the solution was left overnight at room temperature. It was then transferred to a separating funnel and was made alkaline by addition of 5% aqueous KOH. The

* Alternatively, 62% of **2b** was obtained by a modified procedure starting from carbinyl diacetate[13] derived from **1b** (1.7 mmol) and mercaptoacetic acid (4 mmol).

** 2-Mercaptopropanoic acid[14] was obtained by reduction of 2,2′-dithiobispropanoic acid with sodium amalgam in aqueous medium.

solution was shaken with dichloromethane; the aqueous layer was separated and acidified with a few drops of 85% H_3PO_4 and then extracted with dichloromethane. The extract was shaken with water, dried over $MgSO_4$ and evaporated to dryness to give acids **2–4** (Table I).

TABLE I

Characterization data of Fn(CHSXCOOH)$_2$ (**2, 3** and **4**)[a]

Compd. No.	R	X	Yield %	IR / cm^{-1} ν(CH)Fn	ν(CH)aliph.	ν(C=O)
2a	Me	CH_2	57	3060 w	2970 w 2920 w	1687 s
2b	Ph	CH_2	49	3070 w	2950 b	1700 s
2c	*p*–ClC_6H_4	CH_2	50	3080 w	2940 m	1700 s
2d	*p*–MeC_6H_4	CH_2	53	3090 w	2970 w 2905 w	1705 s
2e	*p*–$MeOC_6H_4$	CH_2	54	3080 m	2950 b	1700 s
3a	Me	CH_2CH_2	90	3090 w	2970 m 2930 m	1705 s
3b	Ph	CH_2CH_2	81	3080 w	2970 w 2910 m	1695 s
4a	Me	$CH_2CH(CH_3)$	57	3080 w	2970 m 2920 s 2850 m	1705 s
4b	Ph	$CH_2CH(CH_3)$	51	3100 w	2980 m 2930 m	1705 s

[a]Fn = 1,1'-ferrocenylene.

*ω,ω'-Disubstituted dimethyl ω,ω'-(1,1'-ferrocenylene)bis(3-thiabutanoate) (**5**), -(4-thiapentanoate) (**6**), and -(2-methyl-4-thiapentanoate) (**7**)*

The acids obtained by the above procedure were esterified by treating their methanolic solutions with ethereal diazomethane for 12 h in a refrigerator. After evaporation of solvents, the oily residue was purified by preparative TLC on silica gel with benzene-ethanol as eluent (Tables II, III and IV).

TABLE II

Characterization data of Fn(CHSXCOOMe)$_2$ (**5**, **6** and **7**)[a]

Compd. No.	R	X	Yield %	IR / cm^{-1} ν(CH)Fn	ν(CH)aliph.	ν(C=O)	ν(C–O)
5a	Me	CH_2	60	3080 w	2920 m	1740 s	1140 s
5b	Ph	CH_2	79	3080 w	2955 m	1730 s	1150 s
5c	*p*–ClC_6H_4	CH_2	86	3080 w	2950 m	1730 s	1150 s
5d	*p*–MeC_6H_4	CH_2	73	3080 w	2950 m 2920 m	1732 s	1145 s
5e	*p*–$MeOC_6H_4$	CH_2	85	3080 w	2950 b	1730 s	1150 s
6a	Me	CH_2CH_2	69	3090 w	2930 m	1743 s	1170 s
6b	Ph	CH_2CH_2	57	3080 w	2960 m 2920 m	1730 s	1160 m
7a	Me	$CH_2CH(CH_3)$	50	3070 w	2960 m 2910 s	1730 s	1150 m
7b	Ph	$CH_2CH(CH_3)$	61	3080 w	2860 s	1730 s	1160 m

[a]Fn = 1,1′-ferrocenylene.

TABLE III

Analysis of esters **5**, **6** and **7**

Compd. No.	Molecular formula	M_r	Calcd. (found) / % C	H
5a	$C_{20}H_{26}FeO_4S_2$	450.4	53.34 (53.51)	5.82 (6.02)
5b	$C_{30}H_{30}FeO_4S_2$	574.5	62.72 (62.89)	5.26 (5.16)
5c	$C_{30}H_{28}Cl_2FeO_4S_2$	643.4	56.00 (55.73)	4.39 (4.50)
5d	$C_{32}H_{34}FeO_4S_2$	602.6	63.78 (64.01)	5.69 (5.56)
5e	$C_{32}H_{34}FeO_6S_2$	634.6	60.57 (60.82)	5.40 (5.22)
6a	$C_{22}H_{30}FeO_4S_2$	478.4	55.23 (55.20)	6.32 (6.10)
6b	$C_{32}H_{34}FeO_4S_2$	602.6	63.78 (63.50)	5.69 (5.50)
7a	$C_{24}H_{34}FeO_4S_2$	506.5	56.91 (56.61)	6.77 (6.59)
7b	$C_{34}H_{38}FeO_4S_2$	630.6	64.76 (64.55)	6.07 (5.80)

TABLE IV

^{1}H-NMR spectra of Fn(CH$_c$-S-CH$_a$H$_b$-COOMe)$_2$ (**5**), Fn(CH$_c$-S-C(H$_b$)(H$_a$)-C(H$_b$)(H$_a$)-COOMe)$_2$ (**6**) and Fn(CH$_c$(R)-S-C(H$_b$)(CH$_3$)-CH$_a$-COOMe)$_2$ (**7**)

Compd. No.	Benzene protons		Ferrocene protons	Aliphatic protons H_a	Aliphatic protons H_b	Aliphatic protons H_c	COO*CH$_3$*	CH$_3$
5a	–		4.20 m (8) 4.17 m	3.15 d (4)	3.17 d	3.92 q (2) 3.90 q	3.72 s (6) 3.73 s	1.65 (6, d)
5b	7.34 (10, m)		4.20 m (8) 4.02 m	2.90 d (4)	3.00 d	4.94 s (2) 4.93 s	3.66 (6, s)	–
5c	7.36 (10, m)		4.10 m (8) 4.08 m	2.90 d (4)	3.04 d	5.00 s (2) 4.96 s	3.70 (6, s)	–
5d	7.27 (4, m)	7.13 (4, d)	4.15 m (8) 4.04 m	2.90 (2, d)	3.01 (2, d)	4.93 s (2) 4.89 s	3.67 s (6) 3.68 s	2.34 (6, s)
5e	7.35 (4, m)	6.86 (4, dd)	4.18 d (8) 4.01m	2.92 (2, d)	3.02 (2, d)	4.93 s (2) 4.91 s	3.68 s (6) 3.69 s	3.81 (6, s)

TABLE IV (Continued)

^{1}H-NMR spectra of Fn(CH$_c$-S-CH$_a$H$_b$-COOMe)$_2$ (**5**), Fn(CH$_c$-S-C(H$_b$)(H$_a$)-C(H$_b$)(H$_a$)-COOMe)$_2$ (**6**) and Fn(CH$_c$-S-C(H$_b$)-CH$_a$-COOMe)$_2$ (**7**)

Compd. No.	Benzene protons	Ferrocene protons	Aliphatic protons			$COOCH_3$	CH_3	
			H_a	H_b	H_c			
6a	–	4.14 (8, m)	2.49 (4, t)	2.71 (4, t)	3. 74 (2, q)	3.38 (6, s)	1.64 (6, d)	
6b	7.33 (10, m)	4.09 m 3.99 m (8)	2.41 (4, m)	2.50 (4, m)	4.72 m 4.68 m (2)	3.62 s 3.01 s (6)	–	
7a	–	4.14 m 4.02 m (8)	2.50 (2, m)	2.75 (4, m)	3.70 (1, q)	3.69 s 3.67 s (6)	1,51 d 1.45 d (6)	1.25 d 1.19 d (6)
7b	7.34 (10, m)	4.10 m 4.00 m (8)	2.32 (2, m)	2.59 (4, m)	4.70 m 4.67 m (2)	3.70 s 3.68 s (6)	1.18 (6, d)	

[a]Fn = 1,1'-ferrocenylene.

[b]The signals given in the first row are due to the *meso* form and those in the second row correspond to the racemic form (cases **5** and **6**). Signals due to diastereomeric mixtures of **7** are also indicated when observed. The ratios of *meso*/racemic forms of esters **5** were calculated from the separated singlets of the methine protons: ~1.2 (**5a**), ~2 (**5b, 5c, 5d**), and ~0.8 (**5e**). The geminal coupling constants for methylene protons in compounds **5** (^2J) are *ca.* –15.1 Hz.

Formation of trans-*2-oxa[3]ferrocenophanes (*trans-**8**), [2,2]ferrocenophanes (**9**) and oligomers (**10**)*

A solution of 0.5 mmol of ω,ω'-(1,1'-ferrocenylene)bis(3-thiabutanoic acids) (**2a–2e**) in 10 ml of dichloromethane (dried over P_2O_5), containing 1 ml of TFAA, was stirred for 0.5 h, during which time the initial brown-yellow solution changed to a dark violet hue. The reaction mixture was then transferred

TABLE V

Characterization data of *trans*-2-oxa[3]ferrocenophanes (*trans*-**8**), [2,2]ferrocenophanes (**9**) and oligomers (**10**)

R	Letter	Ethers *trans*-**8**			Dimers **9**	Oligomers **10**
		Yield %	M.p. °C	M.p.$^{lit.}$ °C	Yield %	Yield %
Me	**a**	15	104–106	98–101[6]	9	10
Ph	**b**	29	189–190	197–198[6]	11	15
p-ClC_6H_4	**c**	21	197–199	–	17	18
p-MeC_6H_4	**d**	47	186–188	–	6	7
p-$MeOC_6H_4$	**e**	21	171–172	–	15	11

trans-**8c**, *Anal.* Calcd. for $C_{24}H_{18}Cl_2FeO$ (M_r = 449.1) C: 64.18, H 4.04%; found C 64.30, H 4.32%.
trans-**8d**, *Anal.* Calcd. for $C_{26}H_{24}FeO$ (M_r = 408.3) C: 76.48, H 5.92%; found C 76.69, H 5.79%.
trans-**8e**, *Anal.* Calcd. for $C_{26}H_{24}FeO_3$ (M_r = 440.3) C: 70.92, H 5.49%; found C 71.20, H 5.33%.

TABLE VI

Molecular weight of dimers **9** and oligomers **10**

Letter	Dimers **9**			Oligomers **10**		
	Molecular formula	M_r found	M_r calcd.	Molecular formula	M_r found	M_r calcd.
a	$C_{28}H_{32}Fe_2$	–	480.3	$C_{42}H_{50}Fe_3$	–	722.4
				$C_{56}H_{66}Fe_4$		962.5
b	$C_{48}H_{40}Fe_2$	740	728.6	$C_{72}H_{62}Fe_3$	1250	1088.8
				$C_{96}H_{82}Fe_4$		1459.1
c	$C_{48}H_{36}Cl_4Fe_2$	900	866.3	$C_{72}H_{56}Cl_6Fe_3$	1400	1301.5
				$C_{96}H_{74}Cl_8Fe_4$		1734.7
d	$C_{52}H_{48}Fe_2$	820	784.7	$C_{78}H_{74}Fe_3$	1320	1178.9
				$C_{104}H_{98}Fe_4$		1571.3
e	$C_{52}H_{48}Fe_2O_4$	860	848.7	$C_{78}H_{74}Fe_3O_6$	1390	1274.9
				$C_{104}H_{98}Fe_4O_8$		1699.3

Molecular weights were estimated by the GPC procedure.

to an ice-water mixture containing some ascorbic acid. The products were extracted with dichloromethane, the extract was shaken with 5% aqeous $NaHCO_3$, water, dried over $MgSO_4$ and evaporated to dryness. The mixtures of ferrocenophanes *trans*-**8**, dimers **9** and oligomeric products **10** were separated by TLC using benzene-ethanol as eluent (Tables V, VI, VII, VIII and IX).

8b, MS: *m/z* 380(M^+, 100), 303(12), 299(57), 287(30), 273(21), 226(100), 208(48), 198(40), 190(6), 184(12), 172(45).

9b, MS: *m/z* 728(M^+, 11), 669(5), 640(2), 602(4), 516(10), 380(13), 366(100), 211(23), 120(13).

10b, MS: *m/z* 874(3), 740(5), 728(17), 669(7), 640(3), 602(4), 516(10), 380(10), 366(100), 211(25), 120(14).

TABLE VII

IR spectra of ethers *trans*-**8**, dimers **9** and oligomers **10**

Compd.	ν(CH)Fc	ν(CH)aliph.	ν(C=C)	ν(COC)	
8a	3100 w	2970 m 2930 m 2870 m	–	1160 w 1020 s	815 s
8b	3090 w	2930 w	1605 w 1495 s	1150 w 1030 s	802 s
9b	3085 w	2970 m 2930 m	1602 s 1496 s	–	
10b	3080 w	2960 m 2920 m	1595 s 1505 s	–	
9c	3095 w	2960 m 2920 m	1590 s 1485 s	–	
10c	3085 w	2975 m 2930 m	1600 s 1495 s	–	
8d	3090 w	2920 s 2850 m	1600 m 1490 s	1150 w 1040 s	805 m
9d	3080 w	2970 w 2920 w	1530 s 1480 s	–	
10d	3090 w	2960 m 2920 m	1605 s 1505 s	–	
8e	3080 w	2910 s	1600 s 1500 s	1170 s 1030 s	825 s
9e	3090 w	2960 m 2920 m	1600 s 1505 s	–	
10e	3085 w	2950 m 2920 m	1605 s 1500 s	–	

TABLE VIII

^{1}H-NMR spectra of *trans*-2-oxa[3]ferrocenophanes (*trans*-**8**)

Compd. No.	Benzene protons	Ferrocene protons H(5)	Ferrocene protons H(2)–H(4)	CH	CH_3
8a	–		4.09 (10)		1.53 (6, m)
8b	7.50 m 7.26 m (10)	4.50 (2, m)	4.17 (6, m)	5.03 (2, s)	–
8c[a]	7.48 d 7.40 d (8)	4.69 (2, m)	4.21 (6, m)	5.15 (2, s)	–
8d	7.39 d 7.16 t (8)	4.48 (2, m)	4.16 (6, m)	4.99 (2, s)	2.32 (6, s)
8e	7.40 m 6.87 m (8)	4.50 (2, m)	4.20 (6, m)	5.00 (2, s)	3.79 (6, s)

[a]Recorded as D_6-DMSO solution.

TABLE IX

^{1}H-NMR spectra of dimers **9** and oligomers **10**

Compd. No.	Benzene protons	Ferrocene protons	CH, CH_2	CH_3O	$CH_3C_6H_4$
9b	7.32 (20, m)	4.19 (16, m)	3.55 (6, m)	–	–
10b	7.21 (~36, m)	4.20 (~29, m)	3.60 (~10, m)		
9c	7.30 (16, m)	4.11 (16, m)	3.65 (6, m)	–	–
10c	7.25 (~27, m)	4.20 (~28, m)	3.72 (9, m)		
9d	7.11 (16, m)	4.15 (16, m)	3.65 (6, m)	–	2.30 s 2.32 s (12)
9e	6.80 m 7.30 m (16)	4.32 (16, m)	3.60 (6, m)	3.81 s 3.79 s (12)	–
10e	6.82 m 7.32 m (~28)	4.18 (~29, m)	3.58 (~9, m)	3.82 s 3.78 s 3.77 s (~20)	–

*Cyclization of α,α'-(1,1'-ferrocenylene)bis(arylmethanols) (**1b**, **1c**) into* cis, trans-*1,3-diaryl-2-oxa[3]ferrocenophanes (**8b**, **8c**)*

Solutions of diols **1** (1 mmol) in benzene were shaken in a separating funnel with an aqeous solution of HCl (1:10) for 30 min. The organic layer was washed with water, dried over Na_2SO_4 and then evaporated. The residue was submitted to TLC on silicagel plates, using benzene-hexane mixtures as eluents, to separate *cis-* and *trans-***8**.

The m.p. and spectra of *trans-***8b** (9%, first band), and *cis-***8b** (15%, second band) were identical to those of authentic specimens.[6] Characterization data of *trans-***8c** (8%) and of the specimen prepared by the previous procedure were identical.

*cis-***8c** (17%); IR spectrum, ν_{max}/cm^{-1}: 3099 w (CH)Fc, 3030 w (CH)Ar, 1589 m (C=C)Ar, 1040 m (COC); ^{1}H-NMR spectrum, δ/ppm: 7.44 (m, 8H, C_6H_4); 4.59 (s, 2H, H(5)Fc); 4.22 (m, 6H, H(2) – H(4) Fc); 5.42 (s, 2H, CH).

Anal. Calcd. for $C_{24}H_{18}Cl_2FeO$ (M_r = 449.1): C 64.18, H 4.04%; found C 64.32, H 3.96%.

Acknowledgment. – We are indebted to Mirko Poje Ph. D. for helpful discussions. We thank the Ministry for Science, Technology and Information of Croatia, Zagreb, Republic of Croatia, for partial support through a grant.

REFERENCES

1. S. Lisac and V. Rapić, *J. Organometal. Chem.* **507** (1996) 215.
2. V. Kovač, V. Rapić. I. Sušnik, and M. Šuprina, *J. Organometal. Chem.* **530** (1997) 149.
3. A. Togni and T. Hayashi (Eds.), *Ferrocenes*, Weinheim, VCH, 1995, p. 175.
4. D. Scataru, I. Mazilu, L. Tataru, T. Lixandru, and Cr. Simionescu, *J. Organometal. Chem.* **373** (1989) 245.
5. D. Scataru, I. Mazilu, M. Vata, L. Tataru, A. Vlase, T. Lixandru, and Cr. Simionescu, *J. Organometal. Chem.* **401** (1991) 87.
6. K. Yamakawa and M. Hisatome, *J. Organometal. Chem.* **52** (1973) 407.
7. G. Neshvad, R. M. G. Roberts, and J. Silver, *J. Organometal. Chem* **236** (1982) 237.
8. M. Cais, P. Ashkenazi, S. Dani, and J. Gottlieb, *J. Organometal. Chem* **122** (1976) 403.
9. J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.* **81** (1959) 3484.
10. J. J. Dannenberg, *Angew. Chem.* **87** (1975) 632.
11. A. Lüttringhaus and W. Kullick, *Angew. Chem.* **70** (1958) 438.
12. S. Kovač and V. Rapić, *Croat. Chem. Acta* **64** (1991) 593, and references cited therein.
13. F. S. Arimoto and A. C. Haven, *J. Am. Chem. Soc.* **77** (1955) 6295.
14. Houben-Weyl, *Methoden der organischen Chemie,* E. Müller (Ed.), Vol 9, Stuttgart, Thieme, 1955, p. 23.

SAŽETAK

Priprava i reakcije nekih ω,ω'-(1,1'-ferocenilen)bis(tiaalifatskih kiselina)

Srđan Lisac, Vladimir Rapić, Zoran Zorić i Nevenka Filipović-Marinić

Kondenzacijom nekoliko α,α'-disupstituiranih 1,1'-ferocenilenbiskarbinola (**1**) s merkaptoetan-kiselinom, 3-merkaptopropan-kiselinom ili 3-acetiltio-2-metilpropan-kiselinom u nazočnosti trifluoroctene kiseline pripravljene su u 49–90%-tnom iskorištenju odgovarajuće 1,1'-ferocenilenbistiaalifatske kiseline (**2–4**). Reakcijom tih kiselina s trifluoracetanhidridom nastaje 15–29% *trans*-2-oksa[3]ferocenofana (*trans*-**8**), 7–13% [2,2]ferocenofana (**9**) i 8–15% odgovarajućih etanoferocenilenskih oligomera (**10**). Predloženi su mehanizmi opisanih reakcija.