

## Ferrocene Compounds. XXI. Synthesis of Some $\beta$ -Aryl- $\beta$ -ferrocenylpropionic Acids and $\beta,\beta$ -(1,1'-Ferrocenylene)bis( $\beta$ -arylpropionic Acids)

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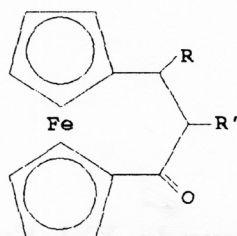
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Reaction of several  $\alpha$ -substituted ferrocenylmethanols **1** with diethyl malonate gave condensation products **3**, which were hydrolyzed and decarboxylated to  $\beta$ -ferrocenylbutyric acid (**6a**) and  $\beta$ -aryl- $\beta$ -ferrocenylpropionic acids (**6b–6e**). Similarly, starting from  $\alpha,\alpha'$ -disubstituted 1,1'-ferrocenylene-bismethanols **2**  $\beta,\beta$ -(1,1'-ferrocenylene)bis(butyric acid) (**11a**) and  $\beta,\beta$ -(1,1'-ferrocenylene)bis( $\beta$ -arylpropionic acids) (**11b–11e**) have been obtained *via* **8** and **9**. The mechanism of these condensation reactions which includes transesterification of diethyl malonate with carbinols **1** and **2** has been proposed.

### INTRODUCTION

It is well known that the action of either polyphosphoric acid or trifluoroacetic anhydride on the  $\omega$ -ferrocenylaliphatic acids gave products with either a heteroannular or a homoannular ring closure or polymers, depending on the aliphatic chain length.<sup>1,2</sup> In this connection, ferrocenepropionic acids and their  $\alpha$ - and/or  $\beta$ -substituted derivatives have been converted into the corresponding [3]ferrocenophane system **I**.<sup>2</sup> On the other hand,  $\beta$ -substituted benzenepropionic acids gave 3-substituted 1-indanones under similar conditions.<sup>3</sup>

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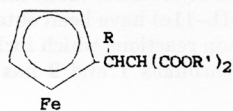
I

Keeping in mind both the possibilities mentioned, we have planned to examine the competitive cyclization reactions of  $\beta$ -phenyl- $\beta$ -ferrocenylpropionic acids and  $\beta,\beta$ -(1,1'-ferrocenylene)bis( $\beta$ -phenylpropionic acids), substituted on the phenyl ring with electron-withdrawing or electron-donating groups.

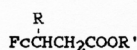
Similar compounds –  $\beta$ -ferrocenylbutyric acid and  $\beta$ -ferrocenyl- $\beta$ -phenylpropionic acid – have been prepared either by condensations of the corresponding ferrocenylcarbinols with diethyl malonate and subsequent hydrolysis and decarboxylation of the diesters obtained<sup>4</sup> or by the Reformatsky reaction of the corresponding acylferrocenes, followed by hydrolysis, dehydration and hydrogenation of the hydroxy-esters formed.<sup>5</sup>



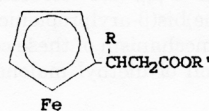
- 3** R' = C<sub>2</sub>H<sub>5</sub>  
**4** R' = H  
**5** R' = CH<sub>3</sub>



- 8** R' = C<sub>2</sub>H<sub>5</sub>  
**9** R' = H  
**10** R' = CH<sub>3</sub>



- 6** R' = H  
**7** R' = CH<sub>3</sub>



- 11**, R' = H  
**12**, R' = CH<sub>3</sub>

- a** R = CH<sub>3</sub>  
**b** R = C<sub>6</sub>H<sub>5</sub>  
**c** R = *p*-ClC<sub>6</sub>H<sub>4</sub>

- d** R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
**e** R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>

Using this procedure,<sup>4</sup> we have prepared  $\beta$ -ferrocenylbutyric acid (**6a**) and  $\beta$ -aryl- $\beta$ -ferrocenylpropionic acids (**6b–6e**) starting from  $\alpha$ -substituted ferrocenylmethanols **1** via malonates **3** and malonic acids **4**. In a similar way, condensation of  $\alpha,\alpha'$ -disubstituted 1,1'-ferrocenylenebismethanols **2** gave  $\beta,\beta$ -(1,1'-ferrocenylene)bis(butyric acid) (**11a**) and  $\beta,\beta$ -(1,1'-ferrocenylene)bis( $\beta$ -arylpropionic acids) (**11b–11e**) via **8** and **9**.

The French paper<sup>4</sup> dealing with condensations of  $\alpha$ -ferrocenylethanol and  $\alpha$ -phenylferrocenylmethanol with sodium salt of diethyl malonate is one of the rare publications dealing with malonic ester syntheses in which carbinols, instead of the usually applied halogenides or tosylates, have been used. For these reactions, the authors supposed the  $S_N1$  mechanism (with leaving of hydroxylic groups from carbinols) because of the high stability of  $\alpha$ -ferrocenylcarbonium ions but they stressed that this explanation is not satisfactory.

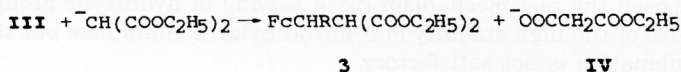
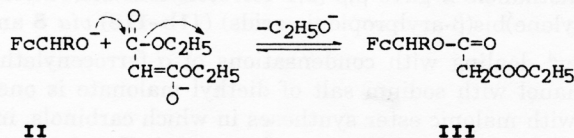
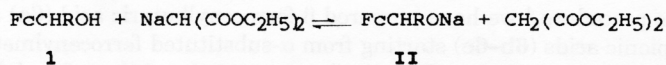
To propose the reaction mechanism of these malonic ester syntheses, we have made several experiments under similar conditions as described in Ref. 4; we used carbinol (or its acetate), sodium and diethyl malonate in molar ratios 1 : 2 : 2–5, first preparing the sodiomalonic ester in xylene and then refluxing it with the condensating component for 1/2–3 hours. We have observed that the reactions of *e.g.*  $\alpha$ -ferrocenylethanol (**1a**) or its acetate with 2 moles of sodiomalonic ester in boiling xylene were completed (according TLC) after 1 1/2 hour. On the other hand, the malonic ester condensations with benzyl alcohol or *n*-butyl alcohol under the described conditions were completed within 2 hours. A 3–5 molar excess of diethyl malonate had no notable effect on the reaction rate.

It can be concluded that, independently of the type of the alcohol used, the condensation products have been formed under similar conditions. Even the reactivities of ferrocenylcarbinol **1a**, and its acetate are practically the same.

It is well known that the hydroxyl group does not leave from ordinary alcohols and its substitution can be performed when it is protonated or converted to a (reactive) ester, because water and acylates are good leaving groups.<sup>6</sup> In this connection, we supposed conversion of carbinols to malonates as intermediates in the reactions performed.

In Ref. 7 base-catalyzed transesterifications of lower malonates (dimethyl, diethyl) with higher alcohols (hexyl, heptyl, benzyl) have been described (*e.g.* transesterification of diethyl malonate with benzyl alcohol in the presence of sodium hydroxide was completed in 2 hours of refluxing with 83% yield). For these conversions, the authors suggested an  $S_N2$  process facilitated by enolization of malonic ester. The relative ease of transesterification of diethyl malonate is also notable from its conversion to dimethyl ester by shaking it in a methanolic solution of potassium methoxide under anhydrous conditions.<sup>8</sup> Keeping in mind these facts, we supposed conversion of carbinol **1** and sodiomalonic ester (enolate) to the corresponding ethyl ferrocyl malonate **III\*** in the first and second reaction steps. The alkoxide **II** needed for this reaction is formed in an (unfavourable) equilibrium between carbinol **1** ( $pK_a \sim 16$ ) and sodiomalonic ester ( $pK_a = 13.5$ ). Ferrocyl malonate formed can then be easily transformed by either  $S_N1$  or  $S_N2$  process to the desired product **3**.

\* ferrocyl = ferrocenylmethyl



Such a pathway is supported by isolation of sodium ethyl malonate (**IV**) from the reaction mixture. The identity of the acid-ester derived from **IV** was confirmed by its comparison with an authentic specimen<sup>9</sup> ( $R_f$  values, IR spectra). An additional support for the mechanism proposed was achieved by the experiments in which reactivity of sodiomalononitrile<sup>10</sup> with carbinols **1** was examined under similar conditions as for the malonic ester synthesis described. In all these experiments, even after prolonged refluxing, only the starting material was isolated, which indicates that for an  $S_N$  conversion of compounds **1** with sodiomalonic acid derivatives these carbinols should be previously esterified.

### EXPERIMENTAL

The m.p.'s were determined with a Reichert Thermovar BT 11 apparatus and are uncorrected. The IR spectra ( $\nu/\text{cm}^{-1}$ ) were recorded as KBr pellets or liquid films with a Perkin-Elmer 257 grating infrared Spectrophotometer.

The  $^1\text{H-NMR}$  spectra ( $\delta$  values; of  $\text{CDCl}_3$  solutions) were recorded on a Varian EM 360 Spectrometer with tetramethylsilane as internal standard. All experiments, except for decarboxylations, were performed under argon. Reaction products were purified by preparative TLC on silica gel (Merck, Kieselgel 60 HF<sub>254</sub>) or by recrystallization from ethanol.

Acylferrocenes<sup>11</sup> and 1,1'-diacylferrocenes<sup>12</sup> were prepared by acylation of ferrocene using the standard methods.  $\alpha$ -Substituted ferrocenylmethanols (**1a-1e**)<sup>13</sup> and  $\alpha,\alpha'$ -disubstituted 1,1'-ferrocenylenebismethanols (**2a-2e**)<sup>14,\*</sup> were obtained by reduction of the corresponding ketones with sodium borohydride.

#### *Diethyl (1-Ferrocenylethyl)malonate (3a) and Diethyl ( $\beta$ -Aryl- $\beta$ -ferrocenyl)isosuccinates (3b-3e)\*\**

820 mg (35 mmole) of molten sodium in dry xylene (30 mL) was converted by shaking in fine dispersion and diethyl malonate (9.6 g, 60 mmole) was added dropwise. The mixture was

\* **2d**, *Anal.* Calcd. for  $\text{C}_{26}\text{H}_{26}\text{FeO}_2$  ( $M_r = 426.3$ ): C 73.25, H 6.15%; found C 73.41, H 6.02%; IR spectrum: 3270 b ( $\nu(\text{O-H})$ ), 3090 w ( $\nu(\text{C-H})\text{Fc}$ ), 2970 and 2920 w ( $\nu(\text{C-H})$  aliph.), 1610 w and 1515 s  $\text{cm}^{-1}$  ( $\nu(\text{C}=\text{C})$  arom.).

**2e**, *Anal.* Calcd. for  $\text{C}_{26}\text{H}_{26}\text{FeO}_4$  ( $M_r = 458.3$ ): C 68.13, H 5.72%; found C 67.93, H 5.97%; IR spectrum: 3320 vb ( $\nu(\text{O-H})$ ) and  $\nu(\text{C-H})\text{Fc}$ ), 2970 and 2920 w ( $\nu(\text{C-H})$  aliph.), 1610 and 1510 s  $\text{cm}^{-1}$  ( $\nu(\text{C}=\text{C})$  arom.).

\*\* isosuccinate = methylmalonate



TABLE I  

$$\begin{array}{c} \text{R} \\ | \\ \text{FcCHCH}(\text{COOC}_2\text{H}_5)_2 \end{array}$$
 Characterization data of  $\text{FcCHCH}(\text{COOC}_2\text{H}_5)_2$  (**3**)

Compd. no.	R	Yield	Colour
		%	
<b>3a</b>	$\text{CH}_3$	—*	red
<b>3b</b>	$\text{C}_6\text{H}_5$	45	orange
<b>3c</b>	$p\text{-ClC}_6\text{H}_4$	60	orange
<b>3d</b>	$p\text{-CH}_3\text{C}_6\text{H}_4$	—*	orange
<b>3e</b>	$p\text{-CH}_3\text{OC}_6\text{H}_4$	56	orange-brown

\* In the work-up procedure diethyl ether was evaporated and xylene solutions were saponified without isolation of the corresponding esters

TABLE II  
 Characterization data of acids **4** and **9**

Compd. no.	R	Yield %	Colour	IR/cm <sup>-1</sup>			
				$\nu(\text{CH})\text{Fc}$	$\nu(\text{CH})\text{aliph.}$	$\nu(\text{C}=\text{O})$	Cp ring**
<b>4a</b>	$\text{CH}_3$	29*	orange-brown resin	3095 w	2915 w	1710 s	990 m 1095 m
<b>4b</b>	$\text{C}_6\text{H}_5$	68	yellow	3080 w	2095 m 2840 w	1710 s	995 m 1105 m
<b>4c</b>	$p\text{-ClC}_6\text{H}_4$	52	orange	3085 w	2900 w	1700 s	995 m 1090 m
<b>4d</b>	$p\text{-CH}_3\text{C}_6\text{H}_4$	71*	yellow-orange	3060 w	2900 w	1700 s	1000 m 1095 m
<b>4e</b>	$p\text{-CH}_3\text{OC}_6\text{H}_4$	57	yellow-orange	3060 w	2920 w	1698 s	1020 m 1090 m
<b>9a</b>	$\text{CH}_3$	51	brown resin	3090 w	2920 w	1750 s	—
<b>9b</b>	$\text{C}_6\text{H}_5$	54*	brown	3070 w	2900 w	1700 s	—
<b>9c</b>	$p\text{-ClC}_6\text{H}_4$	75*	deep brown	3090 w	2910 w	1695 s	—
<b>9d</b>	$p\text{-CH}_3\text{C}_6\text{H}_4$	58*	brown	3090 w	2970 w 2920 w	1700 s	—
<b>9e</b>	$p\text{-CH}_3\text{OC}_6\text{H}_4$	67*	deep brown	3080 w	2960 w 2920 w	1700 s	—

\* Calculated on the basis of the corresponding carbinols **1** and **2**

\*\* Cp = cyclopentadiene (*i.e.* monosubstituted ferrocene derivative)

stirred for 1/2 hour at 110 °C until sodium disappeared. The solution of carbinol **2** (10 mmole) in the same solvent (20 mL) was added. After reflux for 2 hours, the reaction mixture was poured onto crushed ice, extracted with diethyl ether, washed with saturated aqueous solution of sodium chloride, dried over magnesium sulphate, and evaporated to dryness, giving resinous yellow products (Table I).

TABLE III  
Characterization data of esters **5** and **10**

Compd. no.	R	Yield %	Colour	IR/cm <sup>-1</sup>			
				$\nu(\text{C-H})_{\text{Fc}}$	$\nu(\text{C-H})_{\text{aliph.}}$	$\nu(\text{C=O})$	Cp ring
<b>5a</b>	CH <sub>3</sub>	58	yellow oil	3080 w	2940 w 2920 w	1730 s	1010 m 1090 m
<b>5b</b>	C <sub>6</sub> H <sub>5</sub>	73	yellow resin	3100 w	2960 w 2930 w	1760 s	995 m 1005 m
<b>5c</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	66	yellow	3080 w	2990 w 2940 w	1750 s	1000 m 1095 m
<b>5d</b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	90	yellow resin	3070 w	2970 w 2920 w	1735 s	1010 m 1100 m
<b>5e</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	94	yellow resin	3080 w	2985 w 2930 w	1740 s	1010 m 1095 m
<b>10a</b>	CH <sub>3</sub>	50	yellow resin	3095 w	2955 w 2920 w	1730 s	—
<b>10b</b>	C <sub>6</sub> H <sub>5</sub>	63	brown-yellow	3100 w	2960 w 2935 w	1740 s	—

TABLE IV  
Analysis of esters **5** and **10**

Compd. no.	Molecular Formula	<i>M<sub>r</sub></i>	Calcd. (found) / (%)	
			C	H
<b>5a</b>	C <sub>17</sub> H <sub>20</sub> FeO <sub>4</sub>	344.2	59.32 (59.61)	5.86 (5.76)
<b>5b</b>	C <sub>22</sub> H <sub>21</sub> FeO <sub>4</sub>	405.3	65.20 (65.15)	5.22 (5.20)
<b>5c*</b>	C <sub>22</sub> H <sub>21</sub> ClFeO <sub>4</sub>	441.7	59.82 (60.00)	4.80 (4.56)
<b>5d</b>	C <sub>23</sub> H <sub>24</sub> FeO <sub>4</sub>	420.3	65.73 (65.39)	5.75 (5.98)
<b>5e</b>	C <sub>23</sub> H <sub>24</sub> FeO <sub>5</sub>	436.3	63.32 (63.81)	5.54 (5.13)
<b>10a</b>	C <sub>24</sub> H <sub>30</sub> FeO <sub>8</sub>	502.3	57.38 (57.57)	6.02 (5.88)
<b>10b</b>	C <sub>34</sub> H <sub>38</sub> FeO <sub>8</sub>	626.2	65.16 (65.32)	5.47 (5.70)

\* Calcd. for Cl 8.25; found 8.59%

TABLE V

$${}^1\text{H-NMR spectra of Fc-}\overset{\text{R}}{\text{C}}\text{H}_b\text{-CH}_a(\text{COOCH}_3)_2 \text{ (5) and ester (10)}$$

Compd. no	Aromatic protons		Ferrocene protons		Aliphatic protons		COOCH <sub>3</sub>	CH <sub>3</sub>
			unsubst. ring	subst. ring	H <sub>a</sub>	H <sub>b</sub>		
5a	-		4.12 (5 s)	4.07 (1+4 m)		3.31 (1 m)	3.62 3.58 (3 s) (3 s)	1.40 (3 d)
5b	7.35 (5 m)		3.83 (5 s)	3.90 (2 m)	4.09 (1+2 d)	4.40 (1 d)	3.61 3.41 (3 s) (3 s)	-
5c	7.34 (4 m)		3.88 (5 s)	3.93 (2 m)	4.09 (1+2 m)	4.43 (1 d)	3.64 3.46 (3 s) (3 s)	-
5d	7.25 (2 d)	7.14 (2 d)	3.84 (5 s)	3.93 (2 m)	4.06 (1+2 d)	4.37 (1 d)	3.59 3.41 (3 s) (3 s)	2.33 (3 s)
5e	7.31 (2 d)	6.88 (2 d)	3.86 (5 s)	3.94 (2 m)	4.08 (1+2 d)	4.38 (1 d)	3.61 3.42 (3 s) (3 s)	3.79 (3 s)
10a	-		-	4.04 (2+8 m)		3.30 (2 m)	3.70 3.59 (6 s) (6 s)	1.40 (6 d)
10b	7.25 (10 m)		-	3.75 (8 m)	3.96 (2 m)	4.21 (2 dd)	3.57 3.43 (6 s) (6 s)	-

TABLE VI

Characterization data of acids **6** and **11**

Compd. no.	R	Yield %	Decarboxylation temperature °C	IR/cm <sup>-1</sup>			Cp ring
				$\nu(\text{C-H})$ Fc	$\nu(\text{C-H})$ aliph.	$\nu(\text{C=O})$	
6a	CH <sub>3</sub>	56	140	3084 w	2940 w 2900 w	1695 s	1010 m 1095 m
6b	C <sub>6</sub> H <sub>5</sub>	84	98	3095 w	2920 w	1700 s	995 m 1100 m
6c	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	68	160	3060 w	2910 w	1680 s	995 m 1090 m
6d	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	-	140-160	3080 w	2910 m	1698 s	1005 m 1095 m
6e	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	58	147	3090 w	2930 w	1690 s	1000 m 1110 m
11a	CH <sub>3</sub>	57	90-100	3080 w	2960 s 2920 s	1715 s	-
11b	C <sub>6</sub> H <sub>5</sub>	60	100	3090 w	2900 w	1705 s	-
11c	<i>p</i> -ClC <sub>6</sub> H <sub>5</sub>	70	120	3080 w	2960 w 2910 w	1715 s	-
11d	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	62	120-130	3090 w	2920 w	1715 s	-
11e	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	68	130-140	3080 w	2960 w 2920 w	1710 s	-

(1-Ferrocenylethyl)malonic Acid (**4a**),  $\beta$ -Aryl- $\beta$ -ferrocenylisuccinic Acids (**4b-4e**) and Their Methyl Esters **5**

The esters **3** (15–20 mmole) were saponified by refluxing in a mixture of ethanol (70 mL), potassium hydroxide (300 mg) and water (20 mL) during a period of 3–4 hours. Ethanol was evaporated, and the reaction mixture washed with diethyl ether. The aqueous layer was acidified, the product extracted with ether, washed with a saturated solution of sodium chloride, dried, and evaporated to dryness (Table II). The acids obtained were esterified by means of the ethereal solution of diazomethane giving the corresponding methyl esters **5** (Tables III, IV and V).

$\beta$ -Ferrocenylbutyric Acid (**6a**),  $\beta$ -Aryl- $\beta$ -ferrocenyl-propionic Acids (**6b-6e**) and Their Methyl Esters **7**

The finely pulverized dicarboxylic acid **4** was heated in a flask immersed in an oil bath, 10–20 degrees Celsius beneath their melting points, until evolution of CO<sub>2</sub> ceased. The resulting residues were pulverized, extracted with hot solution of potassium hydroxide ( $w = 0.05$ ), and separated by filtering from the insoluble part. The alkaline solution was cooled, washed with ether, acidified with hydrochloric acid ( $w = 0.05$ ), and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulphate, and evaporated to dryness (Table VI). The esterification of the monocarboxylic acids obtained with diazomethane gave methyl esters **7** (Tables VII, VIII and IX).

TABLE VII  
Characterization data of esters **7** and **12**

Compd. no.	R	Yield %	Colour	IR/cm <sup>-1</sup>			
				$\nu(\text{CH})_{\text{Fc}}$	$\nu(\text{CH})_{\text{aliph.}}$	$\nu(\text{C}=\text{O})$	Cp ring
<b>7a</b>	CH <sub>3</sub>	70	yellow oil	3070 w	2940 m 2910 m	1720 s	900 m 1090 m
<b>7b</b>	C <sub>6</sub> H <sub>5</sub>	58	yellow oil	3100 w	2950 w	1760 s	1000 m 1105 m
<b>7c</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	75	yellow	3080 w	2940 w 2905 w	1725 s	1005 m 1095 m
<b>12a</b>	CH <sub>3</sub>	59	yellow resin	3095 w	2950 m 2920 m	1730 s	—
<b>12b</b>	C <sub>6</sub> H <sub>5</sub>	48	yellow resin	3060 w	2910 m	1713 s	—
<b>12c</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	51	orange resin	3090 w	2955 m 2920 m	1735 s	—
<b>12d</b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	55	brown resin	3100 w	2960 m 2920 m	1735 s	—
<b>12d'</b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		brown resin	3100 w	2950 m 2925 m	1710 s	—
<b>12e</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	57	brown resin	3100 w	2960 m 2935 m	1737 s	—
<b>12e'</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		brown resin	3095 w	2965 m 2940 m	1715 s	—

Note: The  $R_f$  values of compounds **12d** and **12e** are slightly higher than the values of compounds **12d'** and **12e'**.



TABLE VIII  
Analysis of compounds **7** and **12**

Compd. no.	Molecular formula	$M_r$	Calcd. (found) / %	
			C	H
<b>7a</b>	$C_{15}H_{18}FeO_2$	286.2	62.96 (63.03)	6.34 (6.21)
<b>7b</b>	$C_{20}H_{20}FeO_2$	348.2	68.99 (68.72)	5.79 (5.94)
<b>7c*</b>	$C_{20}H_{19}ClFeO_2$	383.7	62.61 (62.35)	4.99 (5.18)
<b>12a</b>	$C_{20}H_{26}FeO_4$	386.3	62.18 (63.32)	6.78 (6.51)
<b>12b</b>	$C_{30}H_{30}FeO_4$	510.4	70.59 (70.50)	5.92 (5.78)
<b>12c</b>	$C_{30}H_{28}Cl_2FeO_4$	579.3	62.19 (62.39)	4.87 (4.99)
<b>12d</b>	$C_{32}H_{34}FeO_4$	538.4	71.38 (71.60)	6.01 (5.83)
<b>12d'</b>			71.38 (71.51)	6.01 (6.26)
<b>12e</b>	$C_{32}H_{34}FeO_6$	570.4	67.38 (67.04)	6.01 (6.33)
<b>12e'</b>			67.38 (67.55)	6.01 (3.06)

\* Calcd. for Cl 9.50; found 9.23 %

TABLE IX  
 $^1H$ -NMR spectra of  $Fe-CH_c-CH_aH_b-COOCH_3$  (**7**) and esters **12**

Compd.	Aromatic protons	Aliphatic protons			Ferrocene protons	COOCH <sub>3</sub>	OCH <sub>3</sub>	CH <sub>3</sub>
		H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>				
<b>7a</b>	—	3.00 (1 m)	2.58 (2 m)	—	4.13 (9 s/m)	3.68 (3 s)	—	1.30 (3 d)
<b>7b</b>	7.22 (5 m)	2.85 (1 dd)	3.13 (1 dd)	4.23 (1 dd)	3.97 (4 m)	4.09 (5 s)	3.59 (3 s)	—
<b>7c</b>	7.25 (2 d)	7.13 (2 d)	2.81 (1 dd)	3.14 (1 dd)	4.22 (1 dd)	3.94 (4 m)	4.11 (5 s)	3.61 (3 s)
<b>12b</b>	7.34 (10 m)	2.73 (2 m)	3.01 (2 m)	4.20 (2 d)	4.00 (8 m)	3.56 (6 s)	—	—
<b>12c</b>	7.24 (4 dd)	7.10 (4 dd)	2.75 (2 m)	2.97 (2 m)	4.16 (2 dd)	4.02 (4 m)	3.38 (4 m)	3.59 (6 s)
<b>12d</b>	7.10 (8 m)	2.79 (4 m)	—	—	3.93 (10 m)	3.55 (6 s)	—	2.33 (6 s)
<b>12d'</b>	7.05 (8 m)	2.85 (4 m)	—	—	4.00 (10 m)	3.58 (6 s)	—	2.33 (6 s)
<b>12e</b>	6.95 (8 m)	2.70 (2 m)	2.30 (2 m)	—	3.78 (10 m)	3.56 (6 s)	3.37 (6 s)	—
<b>12e'</b>	6.94 (8 m)	2.70 (2 m)	2.25 (2 m)	—	3.85 (10 m)	3.57 (6 s)	3.76 (6 s)	—

$\beta,\beta$ -(1,1'-Ferrocenylene)bis( $\beta$ -methylisuccinic Acid) (**9a**),  
 $\beta,\beta$ -(1,1'-Ferrocenylene)bis( $\beta$ -arylisuccinic Acids) (**9b-9e**)  
 and Their Methyl Esters **10**

In a similar way as described for the preparation of compounds **3**, esters **8** were obtained starting from sodium (70 mmole), diethyl malonate (120 mmole) and biscarbinols **2** (10 mmole) in boiling xylene. The crude materials containing some xylene were hydrolyzed in an usual manner giving acids **9** (Table II), which were converted by the action of diazomethane to methyl esters **10** (Table V).

$\beta,\beta$ -(1,1'-Ferrocenylene)bis(butyric Acid) (**11a**),  
 $\beta,\beta$ -(1,1'-Ferrocenylene)bis( $\beta$ -arylpropionic Acids) (**11b-11e**)  
 and Their Methyl Esters **12**

According to the procedure for decarboxylation **4**  $\rightarrow$  **6**, the tetracarboxylic acids **9** were converted into dicarboxylic acids **11**. In this case, the filtered alkaline solutions of the potassium salts obtained were cooled and the raw acids precipitated upon acidification with aqueous hydrochloric acid ( $w = 0.1$ ) (Table VI). The physical properties of the corresponding methyl esters **12** are presented in Tables VII, VIII and IX.

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## SAŽETAK

**Sinteza nekih  $\beta$ -aril- $\beta$ -ferocenilpropionskih kiselina i  $\beta,\beta$ -(1,1'-ferocenilen)bis( $\beta$ -arilpropionskih kiselina)***Srdan Lisac, Vladimir Rapić i Spomenka Kovač*

Reakcijom nekoliko  $\alpha$ -supstituiranih ferocenilmetanola **1** s dietil-malonatom dobiveni su kondenzacijski produkti **3** koji su hidrolizirani i dekarboksilirani u  $\beta$ -ferocenilmaslačnu kiselinu (**6a**) i  $\beta$ -aril- $\beta$ -ferocenilpropionske kiseline (**6b-6e**). Na sličan su način iz  $\alpha,\alpha'$ -disupstituiranih 1,1'-ferocenilenbismetanola **2** preko međuprodukata **8** i **9** pripravljene  $\beta,\beta$ -(1,1'-ferocenilen)bis(maslačna kiselina) (**11a**) i  $\beta,\beta$ -(1,1'-ferocenilen)bis( $\beta$ -arilpropionske kiseline) (**11b-11e**). Predložen je mehanizam tih kondenzacijskih reakcija koji uključuje transesterifikaciju dietil-malonata s karbinolima **1** i **2**.