CROATICA CHEMICA ACTA CCACAA **72** (1) 103–113 (1999)

ISSN-0011-1643
CCA-2564 *Original Scientific Paper*

Ferrocene Compounds. XXVI.[#] *C*- and *O*-Ferrocenylalkylation of Methyl Salicylate

Veronika Kovač, Vladimir Rapić, Jasmina Alagić, and Lidija Barišić*

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

Received April 22, 1998; revised October 15, 1998; accepted October 16, 1998

Reaction of equimolar amounts of methyl salicylate, sodium and *N,N,N*-trimethylferrocylammonium iodide (**1a**) in ethanol gave 55% of ethyl 1-ferrocenylethyl ether (**4**). By refluxing a solution of 9 mmol sodium and 3 mmol of $FcCHRNMe_3I$ (**1a**, R = H; **1b**, R = Me; **1c**, R = Ph) in a large excess of methyl salicylate for 2–3 hours, the corresponding methyl 5-ferrocylsalicylates (**5**) (10–23%) and methyl-3-ferrocylsalicylates (**6**) (12–20%) were obtained. During conversion of salt **1b**, besides of **5b** and **6b**, 20% of vinylferrocene (**7**) and 6% of 1-ferrocenylethyl methyl ether (**8**) were isolated. Under the same conditions as in conversions **1** → **5**, **6** 2-ferrocenylethyl acetate (**11**) and methyl salicylate failed to react, and 2-ferrocenylethyl bromide (**12**) was transformed to 12% of methyl *o*-(2-ferrocenylethoxy)benzoate (**13**) and 25% of methyl 5-(2-ferrocenylethyl)salicylate (**14**), as well as 10% of vinylferrocene (**7**). The mechanisms of reactions **1** → **5**, **6** and **12** → **13**, **14** are discussed, suggesting a stabilization effect by ferrocene nucleus in the intermediate α- and β-ferrocenyl carbocations.

INTRODUCTION

In continuation of our programme on the chemistry of ferrocene heteroaliphatic acids,[2–4] we have described the synthesis and reactions of new types of ferrocenyloxaaliphatic acid ester, FcCHROCHR'COOMe (R = H, Me, Ph; R' = H, Me) (**2**).[3] These compounds have been prepared by the reac-

[#] For Part XXV, see Ref. 1

* Author to whom correspondence should be addressed.

tion of alkoxides derived from methyl glycolate or methyl lactate with the corresponding *N,N,N*-trimethylferrocylammonium iodides (**1**)* or ferrocenylcarbinyl acetates. The resultant esters were accompanied by a small quantity of oligomeric esters, $FcCHR(OCHR'CO)_nOMe$, and by some ferrocyl methyl ethers. As opposed to the alkaline hydrolysis of the analogous methyl benzoxyacetate into benzoxyacetic acid, acidification of sodium alkanoates obtained by saponification of esters **2** unexpectedly gave the corresponding ferrocenylcarbinols. In a similar way, esters **2** were converted into mixtures of the mentioned carbinols and diferrocyl ethers by the action of aqueous hydrochloric acid.

It is well known[6] that phenoxides derived from alkyl salicylates, on prolonged heating with arylmethyl halides, gave alkyl *o*-(arylmethoxy)benzoates, the benzene analogues of the ferrocenyloxaaliphatic esters (**2**). *E. g.* by refluxing an equimolar mixture of methyl salicylate, sodium methoxide and benzyl chloride in methanol for eight hours, 78% of methyl *o*-benzoxybenzoate was obtained.[6c] Given this conversion and the interesting properties of esters **2** as well as to study the possible participation of α- and β-ferrocenyl carbocations in these conversions, we undertook to examine the possibility of preparing *o*-$Fc(CH_2)_nCHROC_6H_4COOMe$ (**3**) by S_N-reactions of the appropriate ferrocenes, $Fc(CH_2)_nCHRX$ (n = 0, 1; R = H, Me, Ph; X = leaving group), with *o*-(methoxycarbonyl)phenoxide.

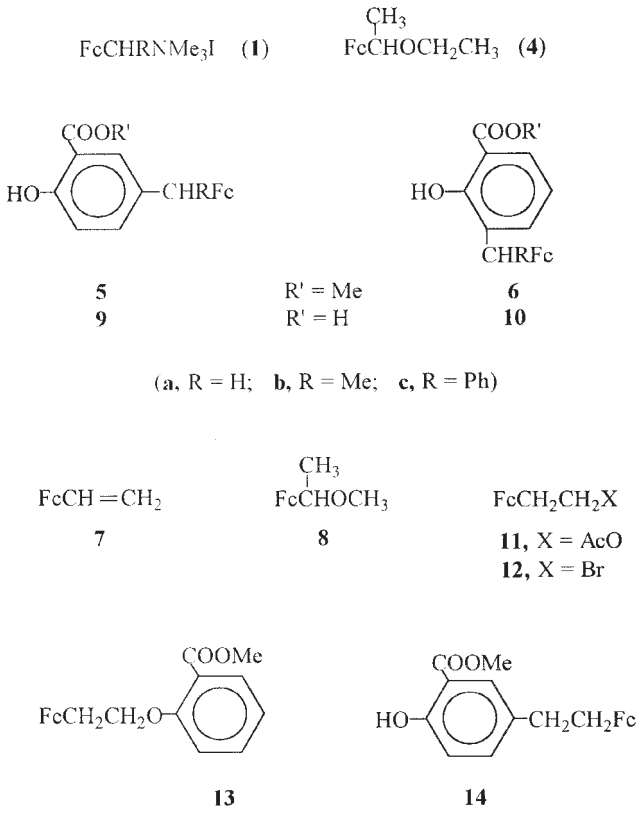
RESULTS AND DISCUSSION

Using the method for the preparation of methyl *o*-benzoxybenzoate (see Introduction)[6c] and a similar procedure for the synthesis of methyl *o*-ferrocylthiosalicylate (starting from methyl thiosalicylate and quaternary salt **1a**)[7] in a reaction of equimolar amounts of methyl salicylate, sodium and iodide **1a** in ethanol, we obtained 55% of ethyl 1-ferrocenylethyl ether (**4**). The desired methyl *o*-ferrocyloxybenzoate (**3**, n = 1, R = H) was not obtained in this reaction. Obviously, despite of the favourable equilibrium phenoxide $\rightleftharpoons$ ethoxide, substrate **1a** was attacked exclusively by the stronger nucleophile, giving most probably the equilibrium controlled product **4**.

Following the procedure for the synthesis of ferrocenyloxaaliphatic esters (**2**),[3] we also prepared phenoxide by dissolving 9 mmol of sodium in a large excess of methyl salicylate and, after adding 3 mmol of the quaternary salt $FcCHRNMe_3I$ (**1a**, R = H; **1b**, R = Me; **1c**, R = Ph), we refluxed the reaction mixture for 2–3 hours. At all reaction stages TLC revealed only two

* ferrocyl = ferrocenylmethyl[5]

substitution products, which were identified as *p*-(**5**) (10–23%) and *o*-ferrocyl substituted phenole (**6**) (12–20%). In contrast to decompositions **2** → ferrocenylcarbinols,[3] it was demonstrated that these esters may be successfully saponified to the corresponding acids **9** or **10**.

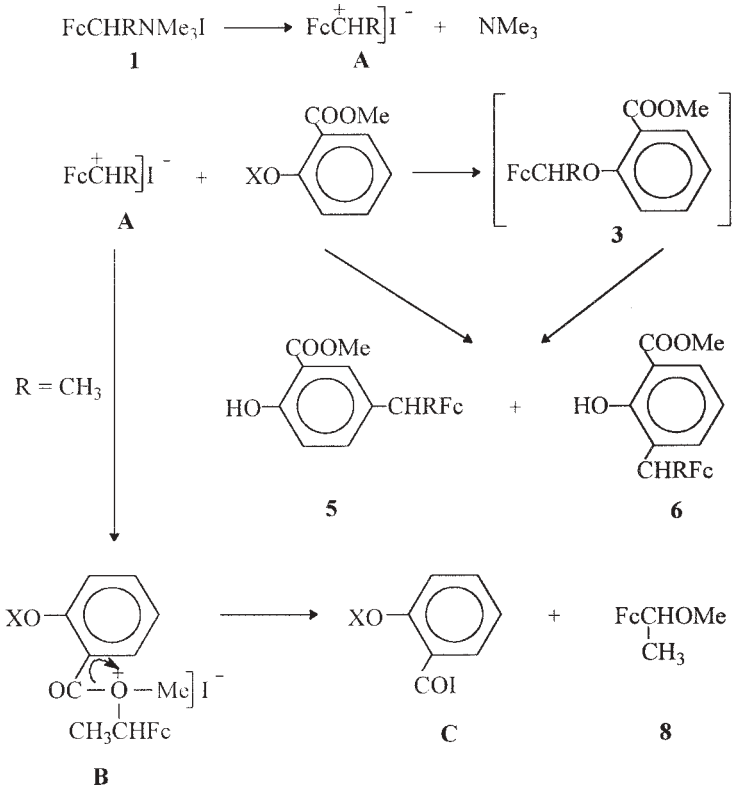


Scheme 1

In the case of salt **1b** conversions, we isolated **5b** (10%) and **6b** (18%), as well as an elimination product **7** (20%) and 1-ferrocenylethyl methyl ether **8** (6%); in neither case was the desired *o*-ferrocyloxybenzoate (**3**) detected. The reactions of **1** with methyl salicylate could take place by mechanisms (Scheme 2) involving the initial formation of well solvated stable ferrocyl carbocations, $Fc\overset{+}{C}HR$ (**A**).[8] Methyl salicylate (or most probably the derived phenoxide) could react with these electrophiles (Lewis acids) as ambident nuchleophile (*i.e.* Lewis base) in terms of formation of **3**, **5**, **6** or **B**. (It is noteworthy that the reaction of iodide **1a** with methyl salicylate in the absence of sodium gave unidentified products of decomposition). It is apparent

that in these competitive reactions, as opposed to conversions of benzene analogues of **1** into *o*-aryloxybenzoates, products of electrophilic substitution of strongly activated benzene ring (**5** and **6**) were formed. The alternative formation of esters **5** and **6** by rearrangement of intermediate ether-esters **3** is hardly possible, since similar transformations of benzene analogues of **3** occur in the presence of (Lewis) acids only.[9]

The overall yields of *p*-(**5**) and *o*-phenols (**6**) are significantly higher (43%) in conversions of **1c** than in those of **1a** (27%) as a consequence of the relative stabilities of the corresponding ferrocyl carbocations $Fc\overset{+}{C}HPh$ > $Fc\overset{+}{C}HMe$ > $Fc\overset{+}{C}H_2$. Yields of **5b**/**6b** (28%) are nearly the same as those of **5a**/**6a** (27%) due to the competitive formation of the elimination product $FcCH{=}CH_2$ (**7**) and ferrocyl methyl ether (**8**). This conversion could be rationalized by initial formation of an oxonium species **B**, which is subsequently cleaved by an AC1-mechanism to give acylium ion (combined with



(X = H or Na; R = H, Me, Ph)

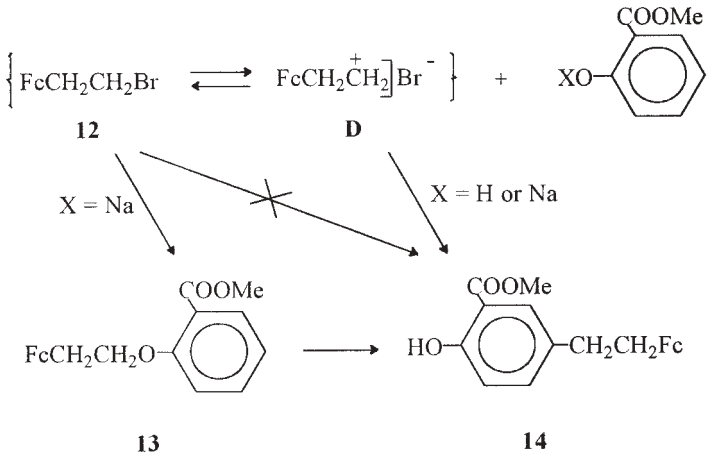
Scheme 2

iodide to **C**) and ether **8**. No formation of analogous methyl ethers was observed in reactions of **1a** and **1c** with methyl salicylate. Different behaviour may be due to an interplay of electronic and steric factors; $Fc\overset{+}{C}HCH_3$ cation is more stable than $Fc\overset{+}{C}H_2$ (derived from **1a**) but not as bulky as $Fc\overset{+}{C}HPh$, and oxonium **B** may be generated in sufficient concentration to give the alternative product **8**.

The capability of ferrocene nucleus to stabilize carbenium ions in a position adjacent to cyclopentadienyl ring is known,[8] but the stabilizing influence of ferrocene to cations in β-position is not well-documented.[10]

The course of reactions of methyl salicylate with 2-ferrocenylethyl acetate (**11**) or bromide (**12**) could indicate possible participation of β-ferrocenyl carbocations.

However, even after prolonged heating under the same conditions as in conversions **1** → **5**, **6**, acetate and methyl salicylate failed to react. The conversion of bromide **12** with methyl salicylate gave 12% of the desired ether-ester **13** and 25% of *p*-substituted phenol **14**, along with 10% of vinylferrocene (**7**). Assuming some stability of β-ferrocenyl carbocation **D**, a dissociative mechanism [similar to conversion **1**(**A**) → **5**, **6** (Scheme 2)] for formation of ester **14** could be proposed (Scheme 3). *o*-(2-Ferrocenylethoxy)benzoate (**13**) is probably formed by S_N2-reaction of bromide **12** with phenoxide derived from methyl salicylate. Rearrangement **13** → **14** is not very probable for the reasons mentioned above. Direct electrophilic alkylation of methyl salicylate by bromide **12**, however, seems unlikely under the reaction conditions because it is well known that the Friedel-Crafts reactions with RX very rarely take place without acidic catalysts.[9]



Scheme 3

The results obtained confirmed again the stability of α-ferrocenyl carbocations. The conversions of 2-ferrocenylethyl bromide indicate that the corresponding β-ferrocenyl carbonium ions, $FcCH_2\overset{+}{C}H_2$, are less stable, though there is a stabilization effect by ferrocene nucleus in these species. The exclusive formation of methyl *o*-(benzoxy)benzoate in the conversion of methyl salicylate with benzyl chloride[6c] suggested the stability order of cations: $Fc\overset{+}{C}H_2 > FcCH_2\overset{+}{C}H_2 > Ph\overset{+}{C}H_2$. These preliminary results on the relative stability of β-ferrocenyl carbonium ions prompt to a further detailed study of the generation and stability of such species in reactions of the appropriate substrates $FcCH_2CHRX$ with methyl salicylates, as well as with $Y(CH_2)_nCOOR$ (Y = OH, SH; n = 1, 2).

EXPERIMENTAL

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}) and by recrystallization from (aqueous) ethanol.

N,N,N-trimethylferrocylammonium iodides (**1**) were prepared by quaternization of the corresponding *N,N*-dimethylferrocylamines with methyl iodide in acetone.[3] Reduction of ferroceneacetic acid[11] with lithium aluminium hydride in diethyl ether gave 89% of 2-ferrocenylethanol,[12] which was brominated with phosphorus tribromide to 66% of 2-ferrocenylethyl bromide (**12**).[13]

*Ethyl 1-ferrocenylethyl ether (**4**)*

A solution of (1.2 g 3 mmol) of **1a** and (456 mg, 3 mmol) of methyl salicylate in (30 mL) of ethanol abs. containing (69 mg, 3 mmol) of sodium was heated under reflux for 8 h. The reaction solution was evaporated to dryness and extracted with diethyl ether. The ethereal extracts were evaporated and purified by preparative TLC (CH_2Cl_2) to give 403 mg (55%) of ethyl ferrocyl ether (**4**). The IR spectra of **4** and of the authentic specimen[14] were identical.

*Methyl 5-ferrocylsalicylates (**5**) and methyl 3-ferrocylsalicylates (**6**)*

Procedure A

207 mg (9 mmol) of sodium was added under mechanical stirring to *ca*. 30 mL of methyl salicylate. After formation of sodium phenoxide, quaternary salts **1** (3 mmol) were added and the reaction mixture refluxed for 2–3 h, whereby the yellow colour changed to brown. The mixture was cooled to room temperature, poured into 10 mL of 5% aqueous sodium hydroxide and extracted with diethyl ether. The ethereal layer was thoroughly washed with saturated aqueous solution of sodium chloride, dried over $MgSO_4$ and evaporated to dryness to give yellow-brownish resinous prod-

ucts, which were separated into esters **2** and **3** by preparative thin layer chromatography using the mixture petroleum ether / benzene (3:2) as eluents (Tables I and II). In the conversion with quaternary salt **1b**, 20% of vinylferrocene (**7**)[15] and 6% of 1-ferrocenylethyl methyl ether (**8**)[3] were isolated as by-products. The IR and ^{1}H NMR spectra of **7** and **8** were identical to the authentic specimens.

Procedure B

A solution of 1.2 g (3 mmol) of iodide **1a** in 10 mL of methyl salicylate was refluxed for 3 h. Thereby the orange colour turned brownish. TLC monitoring showed gradual decomposition of the starting material into an unidentified dark product.

*5-Ferrocylsalicylic acid (**9**) and 3-ferrocylsalicylic acid (**10**)*

A solution of 0.1 mmol of ester **5c**, **6a** or **6c** in 10 mL of ethanol, containing 20 mg (0.5 mol) of sodium hydroxide and one drop of water, was refluxed for 3 h. Ethanol was evaporated, the residue diluted with water and washed with diethyl ether, yielding an alkaline solution of sodium salicylate. This was acidified with aqueous hydrochloric acid (16%) to pH ~ 1 and extracted with ether to yield bright yellow crystalline acids **9** or **10** on evaporation of the solvent.

9c (51%); IR spectrum (KBr) ν_{max}/cm^{-1}: 2979 b (OH) COOH, 1661 s (C=O) COOH, 1224 s (C-O) COOH.

Anal. Calcd. for $C_{24}H_{20}FeO_3$ (M_r = 412.3): C 69.92, H 4.89%; found C 70.15, H 5.20%.

10a (62%); IR spectrum (KBr) ν_{max}/cm^{-1}: 3000 b (OH) COOH, 1640 s (C=O) COOH, 1240 s (CO) COOH.

Anal. Calcd. for $C_{18}H_{16}FeO_3$ (M_r = 336.2): C 64.31, H 4.80 %; found C 64.02, H 5.04%.

10c (73%); IR spectrum (KBr) ν_{max}/cm^{-1}: 2992 b (OH) COOH, 1656 s (C=O) COOH, 1237 s (CO) COOH.

Anal. Calcd. for $C_{24}H_{20}FeO_3$ (M_r = 412.3): C 69.92, H 4.89%; found C 69.68, H 5.07%.

*2-Ferrocenylethyl acetate (**11**)*

To a solution of 1.0 g (4.3 mmol) of 2-ferrocenylethanol in 25 mL of benzene abs. 0.44 g (4.3 mmol) of acetic anhydride was added. The reaction solution was refluxed for 2 h, and evaporated *in vacuo* to yield 0.99 g (85%) of acetate **11**.

IR spectrum ($CHCl_3$), ν_{max}/cm^{-1}: 3098 w (C-H) Fc, 2975 w, 2929 w and 2859 w (C-H) aliph., 1742 s (C=O) acetate, 1235 s d (C-O). ^{1}H NMR spectrum ($CDCl_3$), δ/ppm: 4.12 (s, 5H, unsubst. Fc ring); 4.19 (t, 2H) and 4.08 (t, 2H) (subst. Fc ring); 3.87 (t, 2H, CH_2O); 2.67 (t, 2H, FcCH_2) and 2.06 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{16}FeO_2$ (M_r = 272.1): C 61.79; H 5.93%; found C 62.01, H 5.69%.

TABLE I

Physical constants and IR spectral data for methyl 5-ferrocylsalicylates (**5**) and methyl 3-ferrocylsalicylates (**6**)

Compd. No.	R	Formula (M_r)	Yield	M.p.	Analysis calcd. (found) / %		IR / cm^{-1}			
			%	°C	C	H	ν(CH) arom.	ν(CH) aliph.	ν(OH)	ν(C=O)
5a	H	$C_{19}H_{18}FeO_3$ (350.1)	15	resin	65.17 (64.94)	5.18 (5.20)	3097 w	2978 m 2953 w 2867 m	3221 b	1682 s
5b	Me	$C_{20}H_{20}FeO_3$ (364.2)	10	resin	69.95 (69.95)	5.53 (5.79)	3105 w	2972 m 2940 w 2878 m	3219 b	1681 s
5c	Ph	$C_{25}H_{22}FeO_3$ (426.3)	23	resin	70.44 (70.49)	5.20 (5.00)	3093 w 3030 w	2970 w 2954 w 2858 w	3206 b	1680 s
6a	H	$C_{19}H_{18}FeO_3$ (350.1)	12	resin	65.17 (65.28)	5.18 (5.30)	3098 m	2975 w 2954 m 2850 w	3195 b	1678 s
6b	Me	$C_{20}H_{20}FeO_3$ (364.2)	18	103.6	69.95 (69.51)	5.53 (5.68)	3099 w	2978 m 2920 w 2868 m	3183 b	1678 s
6c	Ph	$C_{25}H_{22}FeO_3$ (426.3)	20	132.8	70.44 (70.18)	5.20 (5.35)	3100 w 3030 w	2970 w 2954 w 2867 m	3162	1677 s

TABLE II

^{1}H-NMR spectral data (δ ppm) for salicylates **5** and **6**

Compd. No.	Benzene protons					Ferrocene protons		Aliphatic protons				OH
	H–3	H–4	H–5	H–6	H–2'–6'	unsubst. ring	subst. ring	CH_3	CH_2	CH	OCH_3	
5a	6.88 (1, d)	7.40 (1, dd)	–	7.70 (1, d)	–	4.14 (5, s)	4.08 m 4.12 m (4)	–	3.68 (1, s)	–	3.95 (3, s)	10.58 (1, s)
5b	6.86 (1, d)	7.38 (1, dd)	–	7.68 (1, d)	–	4.15 (5, s)	4.07 m 4.22 m (4)	1.56 (3, d)	–	3.93 q (4)	3.94 s	10.58 (1, s)
5c	7.03 (1, d)	7.51 (1, dd)	–	7.88 (1, d)	7.37 (5, m)	4.16 (5, s)	4.09 m 4.31 m (4)	–	–	5.38 (1, s)	4.05 (3, s)	10.76 (1, s)
6a	–	7.40 (1, d)	6.84 (1, t)	7.69 (1, dd)	–	4.14 (5, s)	4.06 m 4.18 m (4)	–	3.73 (3, s)	–	3.95 (3, s)	11.16 (1, s)
6b	–	7.19 (1, d)	6.80 (1, t)	7.66 (1, dd)	–	4.16 (5, s)	4.08 m 4.29 m (4)	1.57 (3, d)	–	4.39 (1, q)	3.96 (3, s)	11.26 (1, s)
6c	–	7.30 (1, dd)	6.99 (1, t)	7.84 (1, dd)	7.40 (5, m)	4.14 (5, s)	4.20 m 4.30 m (4)	–	–	5.78 (1, s)	4.07 (3, s)	11.40 (1, s)

*Methyl o-(2-ferrocenylethoxy)benzoate (**13**) and methyl 5-(2-ferrocenylethyl)salicylate (**14**)*

Procedure A

In a similar way as described in procedure 3.1., a mixture of 207 mg (9 mmol) of sodium, 30 mL of methyl salicylate and 816 mg (3 mmol) of acetate **11** was refluxed for 2–10 h. The work-up afforded only unchanged starting material.

Procedure B

Starting with the same quantity of sodium and methyl salicylate as above, 879 mg (3 mmol) of bromide **12** was added. After standing overnight and refluxing for 6 h the reaction mixture was worked up as described. The yellow-brownish resinous mixture separated by preparative TLC (CH_2Cl_2) gave 64 mg (10%) of vinylferrocene (**7**) 131 mg (12%) of benzoate **13** and 273 mg (25%) of salicylate **14**.

13; IR spectrum (CH_2Cl_2), ν_{max}/cm^{-1}: 3104 w (C-H) arom., 2941 m, 2881 w and 2849 w (C-H) aliph., 1734 s (C=O) COOMe, 1252 s (C-O) COOMe. ^{1}H NMR spectrum ($CDCl_3$), δ/ppm: 6.97 (m, 1H, H–3 Ph); 7.41 (m, 1H, H–4 Ph); 6.93 (m, 1H, H–5 Ph); 7.77 (m, 1H, H–6 Ph); 4.15 (b m, 11H, Fc and CH_2O); 2.86 (t, 2H, FcCH_2) and 3.90 (s 3H, CH_3O).

Anal. Calcd. for $C_{20}H_{20}FeO_3$ (M_r = 364.2): C 65.95; H 5.53%; found C 66.12, H 5.38%.

14; IR spectrum (CH_2Cl_2), ν_{max}/cm^{-1}: 3193 b (OH), 3103 w (C-H) arom., 2955 m, 2927 w and 2856 w (C-H) aliph., 1979 s (C=O) salicylate, 1251 s (C-O) salicylate. ^{1}H NMR spectrum ($CDCl_3$), δ/ppm: 11.02 (s, 1H, OH); 6.77 (d, 1H, H–3 Ph); 7.31 (d, 1H, H–4 Ph); 7.68 (d, 1H, H–6 Ph); 4.15 (m, 9H, Fc); 3.98 (t, 2H, PhCH_2); 3.93 (s, 3H, CH_3O) and 2.81 (t, 2H, FcCH_2).

Anal. Calcd. for $C_{20}H_{20}FeO_3$ (M_r = 364.2): C 65.95; H 5.53%; found C 65.70, H 5.69%.

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

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SAŽETAK

C- i *O*-ferocenilalkiliranje metil-salicilata

Veronika Kovač, Vladimir Rapić, Jasmina Alagić i Lidija Barišić

Reakcijom ekvimolarnih količina metil-salicilata, natrija i *N, N, N*-trimetilferocil-amonijeva jodida (**1a**) u etanolu dobiveno je 55% etil-1-feroceniletil-etera (**4**). Refluksiranjem otopine 9 mmol natrija i 3 mmol FcCHRNMe$_3$I (**1a**, R = H; **1b**, R = Me; **1c**, R = Ph) u velikom suvišku metil-salicilata tijekom 2–3 sata, nastaju odgovarajući metil-5-ferocilsalicilati (**5**) (10–23%) i metil-3-ferocilsalicilati (**6**) (12–20%). Prigodom pretvorbe soli **1b**, osim **5b** i **6b**, izolirano je 20% vinilferocena (**7**) i 6% 1-feroceniletil-metil-etera (**8**). Pri uvjetima pretvorbi **1** → **5, 6** 2-feroceniletil-acetat (**11**) i metil-salicilat ne reagiraju, a 2-feroceniletil-bromid (**12**) preveden je u 12% metil-*o*-(2-ferociletoksi)benzoata (**13**) i 25% metil-5-(2-feroceniletil)salicilata (**14**), te 10% vinilferocena (**7**). Predložen je mehanizam reakcija **1** → **5, 6** i **12** → **13, 14** iz kojega je vidljiv stabilizacijski utjecaj ferocenske jezgre na intermedijarne α- i β-ferocenilne karbokatione.