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Synthesis of [7] Ferrocenophane Derivatives

Akira KASAHARA, Taeko IZUMI, Emi YAHAGI, and Yoshio KAMEI

Department of Applied Chemistry, Faculty of Engineering,

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Abstracts

The internal Michael addition reaction of 1,1'-dicinnamoyl-ferrocene with active methylene compound such as diethyl malonate proceeded to the formation of 3,5-diphenyl-4,4-diethoxycarbonyl-1,7-dioxo[7]ferrocenophane.

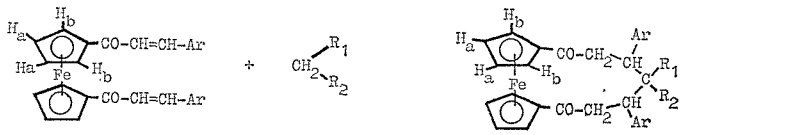
Introduction

In marked contrast to the active interest shown generally in bridged ferrocene compounds,[1] the [7]ferrocenophane system has received little attention and only one compound of this type has been described: Toma and Salsova[2] reported that an intramolcular Michael addition reaction of 1-(*p*-chlorocinnamoyl)-1'-(3-oxobutyl)-ferrocene led to the formation of 3-(*p*-chlorophenyl)-1,5-dioxo[7]ferrocenophane. As a part of our studies on metallocenophane chemistry, the main goal of the present study was to examine the possibility of using internal Michael addition reaction of 1,1'-dicinnamoylferrocene with active methylene compounds such as diethyl malonate to synthesise [7]ferrocenophane derivatives.

Results and Discussion

In the presence of potassinm *t*-butoxide, the reaction of 1,1'-dicinnamoylferrocene (**1**) with diethyl malonate (**2a**) in *t*-butanol gave very high yields of 4,4-diethoxycarbonyl-3,5-diphenyl-1,7-dioxo[7]ferrocenophane[3] (**3a**). Under the same conditions, the internal Michael addition reaction of **1** with ethyl acetoacetate (**2b**) and ethyl cyanoacetate (**2c**) gave rise to the formation of 4-acetyl-4-ethoxycarbonyl-3,5-diphenyl-1,7-dioxo[7]ferrocenophane (**3b**) and 4-cyano-4-ethoxycarbonyl-3,5-diphenyl-1,7-dioxo[7]ferrocenophane (**3c**), respectively. Furthermore, the condensation of 1,1'-bis(*p*-methylcinnamoyl)ferrocene (**4**) with active methylene compounds (**2a-c**) also led to the formation of 4,4-diethoxy-

carbonyl-3,5-di-*p*-tolyl-1,7-dioxo[7]ferrocenophane (**5a**), 4-acetyl-4-ethoxy-carbonyl-3,5-di-*p*-tolyl-1,7-dioxo[7]ferrocenophane (**5b**), and 4-cyano-4-ethoxycarbonyI-3,5-di-*p*-tolyl-1,7-dioxo[7]ferrocenophane (**5c**), respectively (see Table 1). The structure of these compounds (**3a-c** and **5a-c**) was established by the observation of IR, NMR, and mass spectra and the elemental analyses. For example, in the IR spectrum of the compound **3a**, the intense bands at 1737 and 1665 cm^{-1} can be assigned to the C=O streching vibrations of -COOEt and Fc-CO- groups, respectively. On the other hand, the NMR spectrum of the compound **3a** showed signals at δ 0.84 (-COOCH$_2$C**H**$_3$), 1.21 (-COOCH$_2$C**H**$_3$), 3.13 (-C**H**-Ph), 3.78 (FcCOC**H**$_2$-), 3.95 (-COOC**H**$_2$CH$_3$), 4.22 (-COOC**H**$_2$CH$_3$), 4.46 (Fc-**H**), 4.72 (Fc-**H**), and 7.12−7.53 *ppm* (Ar-**H**). The peaks at 0.84 and 1.21 *pp*m in this spectrum are assigned to the methyl protons of ester groups and the peaks at 3.95 and 4.22 *ppm* also to the methylene protons of ester groups. The nonequivalence of these methyl and methylene groups is most easily explained in term of a cyclic system in which [7] ferrocenophane system is involved. In the NMR spectrum of **5a**, the same phenomena were also observed.



1 : Ar=-Ph
4 : Ar=-p-Tolyl

2_a : R_1=R_2=-COOEt
2_b : R_1=-$COCH_3$
R_2=-COOEt
2_c : R_1=-COOEt
R_2=-CN

3_a : Ar=-Ph
R_1=R_2=-COOEt
3_b : Ar=-Ph
R_1=-$COCH_3$; R_2=-COOEt
3_c : Ar=-Ph
R_1=-COOEt; R_2=-CN
5_a : Ar=-p-Tolyl
R_1=R_2=-COOEt
5_b : Ar=-p-Tolyl
R_1=-$COCH_3$; R_2=-COOEt
5_c : Ar=-p-Tolyl
R_1=-COOEt; R_2=-CN

Fig. 1

Experimental

Meterials. All the melting points are uncorrected. 1,1'-Dicinnamoylferrocene (**1**) was prepared according to the method described by Mashburn *et al.*[4]

Measurements. The NMR spectra were determined in $CDCl_3$ with a Hitachi

R-22 spectrometer, using TMS as an internal standard. The IR spectra were measured using KBr disks with a Hitachi 215 spectrophotometer. The mass spectra were obtained on a Hitachi RMU-6M nass spectrometer, using a direct insertion probe at an ionization energy of 70 eV.

Synthesis of **1.1'-*bis*-*p*-*methylcinnamoyl*ferrocene** (**1**). In the presence of sodium hydroxide (6 g, 0.15 mol) in a mixture of ethanol (100 ml) and water (75 ml), p-tolualdehyde (14.4 g, 0.12 mol) was reacted with 1,1'-diacetylferrocene (5.4 g, 0.02 mol) in ethanol (50 ml) under N_2 atmosphere. After stirring at room temperature for 6 h, the resulting reddish precipitate was filtered off, washed with water, dried, and recrystallized from ethanol to give 3.6 g (38%) of the red crystals of 1,1'-bis-*p*-methylcinnamoylferroeene (4), mp 212–214°C IR: 1650 (C=O), 965 cm^{-1} (trans -CH=CH-). NMR: δ 2.31 (s, 6H, $-CH_3$), 4.64 (m, 4H, Fc-H_a), 4.29 (m, 4H, Fc-H_b), 7.00 (d, 2H, -CO-CH=C-, J=16 Hz), 7.15 (d, 4H, Ar-H, J=8 Hz), 7.49 (d, 4H, Ar-H, J=8 Hz), 7.76 *ppm* (d, 2H, -C=CH-Ar, J=16 Hz). MS: m/e 474 (M^+). Found: C, 75.74; H, 5.37%. Calcd for $C_{30}H_{20}O_2Fe$: C, 75.95; H, 5.52%; mol wt, 474.

General procedure for the synthesis of 3,5-diaryl-1,7-dioxo[7]ferrocenophane derivatives (**3** and **5**). The active methylene compound (2_{a-c}) (11 mmol) was added to a solution of potassium (0.13 g, 3.3 mmol) in dry *t*-butanol (20 ml). To the reaction mixture was dropwise added 10 mmol of **1** or **4** at 30°C under N_2 atmosphere. After stirring at 50°C for 6 h, the reaction mixture was then concentrated under reduced pressure and the residue was extracted with $CHCl_3$, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Column separation (SiO_2) of the residue and recrystallization from ethanol gave the product (**3** or **5**) as reddish crystals. The results and the properties of the products are listed in Table1, 2, and 3.

Table 1. The reaction of 1,1'-cinnamoylferrocene derivatives (**1** or **4**) with active methylene compounds (2_{a-c}).

Active methylene compound	Product (yield)	Mp°C	Formular	Analyses Found (Calcd %) C	H	N	MS: m/e M^+
a) Reaction with 1,1'-cinnamoylferrocene (**1**).							
2_a	3_a	93–94	$C_{35}H_{34}FeO_6$	68.86	5.47		606
	(82%)			(69.14)	(5.65)		(606)
2_b	3_b	134–135	$C_{34}H_{32}FeO_5$	70.67	5.41		576
	(81%)			(70.84)	(5.59)		(576)
2_c	3_c	226–227	$C_{33}H_{29}FeNO_4$	70.65	5.11	2.43	559
	(67%)			(70.83)	(5.22)	(2.50)	(559)

b) Reaction with 1,1'-bis(p-methylcinnamoyl)ferrocene (**4**).

2_a	5_a	111−113	$C_{37}H_{38}FeO_6$	69.89	5.91		634
	(85%)			(70.03)	(6.03)		(634)
2_b	5_b	142−144	$C_{36}H_{34}FeO_5$	71.63	5.61		602
	(72%)			(71.76)	(5.68)		(602)
2_c	5_c	230(dec)	$C_{35}H_{33}FeNO_4$	71.49	5,60	2.31	587
	(62%)			(71.55)	(5.66)	(2.38)	(587)

Table 2. Characteristic IR frequencies of the products.

Compound	Cp ring 810 cm^{-1}	$COCH_2$-	Ar	COFc	$COCH_3$	COOEt	CN
3_a	815	1430	1595 760 690	1665		1737	
3_b	810	1420	1600 760 690	1670	1710	1740	
3_c	810	1420	1600 760 690	1665		1740	2240
5_a	810	1415	1600 800	1670		1735	
5_b	810	1420	1600 800	1670	1710	1740	
5_c	810	1420	1600 800	1665		1740	2220

Tadle 3. The NMR spectra of the products (δ, *ppm*).

Compound

3a : 0.84 (t, 3H, -$COOCH_2CH_3$), 1.21 (t, 3H, -$COOCH_2CH_3$), 3.13 (m, 2H, -CHAr), 3.72 (m, 4H, $FcCOCH_2$-), 3.95 (q, 2H, -$COOCH_2CH_3$), 4.22 (q, 2H, -$COOCH_2CH_3$), 4.46 (m, 4H, Cp-H_a), 4.72 (m, 4H, Cp-H_b), 7.12−7.73 (m, 10H, Ar-H).

3b : 0.93 (t, 3H, -$COOCH_2CH_3$), 2.25 (s, 3H, -$COCH_3$), 3.23 (m, 2H, -CHAr), 3.71 (m, 4H, $FcCOCH_2$-), 4.04 (q, 2H, -$COOCH_2CH_3$), 4.43 (m, 4H, Cp-H_a), 4.58 (m, 4H, Cp-H_b), 7.18−7.42 (m, 10H, Ar-H).

3c : 0.80 (t, 3H, -$COOCH_2CH_3$), 3.46 (m, 2H, -CHAr), 3.68 (m, 4H, $FcCOCH_2$-), 3.84 (q, 2H, -$COOCH_2CH_3$), 4.58 (m, 4H, Cp-H_a), 4.94 7.21−7.38 (m, 10H, Ar-H).

5a : 1.01 (t, 3H, -$COOCH_2CH_3$), 1.23 (t, 3H, -$COOC_2H_2CH_3$), 2.24 (s, 3H. Ar-CH_3), 2.40 (s, 3H, Ar-CH_3), 3.17 (m, 2H, -CHAr), 3.74 (m, 4H, $FcCOCH_2$-), 3.92

(q, 2H, -COOC**H**$_2$CH$_3$), 4.24 (q, 2H, -COOC**H**$_2$CH$_3$), 4.47 (m, 4H, Cp-**H**$_a$), 4.74 (m, 4H, Cp-**H**$_b$), 7.07 (d, 4H, Ar-H), 7.61 (d, 4H, Ar-**H**).

5b : 0.94 (t, 3H, -COOCH$_2$C**H**$_3$), 2.18 (s, 3H, -COC**H**$_3$), 2.25 (s, 3H, Ar-C**H**$_3$), 2.42 (s, 3H, Ar-C**H**$_3$), 3.18 (m, 2H, -C**H**Ar), 3.68 (m, 4H, FcCOC**H**$_2$-), 4.02 (q, 2H, -COOC**H**$_2$CH$_3$), 4.42 (m, 4H, Cp-**H**$_a$), 4.68 (m, 4H, Cp-**H**$_b$), 7.10 (d, 4H, Ar-**H**), 7.42 (m, 4H, Ar-**H**).

5c : 0.81 (t, 3H, -COOCH$_2$C**H**$_3$), 2.25 (s, 3H, Ar-C**H**$_3$), 2.30 (s, 3H, Ar-C**H**$_3$), 3.14 (m, 2H, -C**H**Ar), 3.81 (q, 2H, -COOC**H**$_2$CH$_3$), 4.16 (m, 4H, FcCOC**H**$_2$-), 4.61 (m, 4H, Cp-**H**$_a$), 4.94 (m, 4H, Cp-**H**$_b$), 7.09 (d, 4H, Ar-**H**), 7.38 (d, 4H, Ar-**H**).

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〔7〕フェロセノファン誘導体の合成

笠原　晃・泉 多恵子・矢作 恵美・亀井 善夫

工学部　応用化学科

t－ブタノール中，塩基の存在での1，1′－ジシンナモイルフェロセンとマロン酸エチルとの反応は分子間マイケル付加反応を起し，4，4′－ジエトオキシカルボニル－3，5－ジフェニル－1，7－ジオキソ[7]フェロセノファンを高収率で生じた。アセト酢酸エチル，シアノ酢酸エチルの様な活性メチレン化合物でも，同じようなマイケル反応を起し[7]フェロセノファン誘導体を生じた。