

MICHAEL ADDITIONS TO METALLOCENE ANALOGUES OF CHALCONES

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Eleven analogues of chalcones were synthesized; the variously substituted ferrocenyl, ruthenocenyl or η^5 -cyclopentadienyltricarbonylmanganese are attached to the β -carbon of the chalcone double bond. Methyl malonate was added to eight selected chalcones. The effect of an aryl group on the chemical shift difference of diastereotopic $-\text{COOCH}_3$ groups is discussed. The Vilsmeier-Haack formylation was employed to prepare 1'-chloro and 1'-bromoferrocenecarbaldehydes. The synthesis of 2-chloroferrocenecarbaldehyde from 2-chloroferrocenylmethylidimethylamine is also described.

The effect of steric factors on the intramolecular cyclization of 1-acyl-1'-cinnamoylferrocenes was investigated in one of our previous papers¹. Examination of Michael addition of methyl malonate to variously substituted η^6 -benzenetricarbonylchromium analogues of chalcone showed² that in certain cases the addition follows a stereospecific course from the *trans* position towards the $\text{Cr}(\text{CO})_3$ group, this being rationalized by steric requirements of this group,

This project was aimed to prepare metallocene analogues of chalcones differing in the steric requirements of the metallocene moiety ML_3 thus enabling to test the importance of steric effects on the activation parameters of the Michael addition and on the spectral properties of the products.

The metallocene analogues of chalcones were obtained in 60–93% yields by the sodium hydroxide catalyzed Claisen-Schmidt condensation of the respective metallocene carbaldehydes with acetophenone in aqueous methanol (Table I). All products prepared had the *trans* configuration at the $\text{C}=\text{C}$ double bond ($J_{\text{AB}} \sim 15$ Hz, Table II). Some problems were encountered with the preparation of η^5 -cyclopentadienyltricarbonylmanganese, which is very photosensitive and undergoes an easy decomposition. $[m]$ Ferrocenophane analogues VIII and IX were prepared by a Friedel-Crafts benzylation of $[m]$ ferrocenophane analogues of chalcones IV and V. Since the starting chalcone are easily oxidized, the conversion of benzylation was low, and therefore the structure elucidation had to be backed by the R_F values and by analogy with other acylations of ferrocene and ruthenocene analogues of chalcones^{3–5}. It was proved that predominantly substitution products at the chalcone

double bond were formed. The easiness of oxidation of [*m*]ferrocenophane analogues of chalcones, as well as the preferential benzoylation to α -position of the double bond was evoked by the electron-donating properties of the methylene bridges, since benzoylation of the chalcone made no problems.

The greatest problems were encountered when attempting to synthesize 3-(2-chloroferrocenyl)-1-phenylpropenone (XI) and 3-(2-bromoferrocenyl)-1-phenylpropenone; these compounds were necessary to prepare for comparison of the effect of halogens bound to positions 1'- and 2- of the ferrocene skeleton. All metallocene-carbaldehydes, including 1'-chloro and 1'-bromoferrocene-carbaldehyde, could be prepared by the Vilsmeier-Haack formylation; nonetheless, this method failed with

TABLE I
1-Phenyl-3-metallocenyl-2-propenones

Compound	Formula (M_r)	Calculated/found		M.p., °C (Yield, %)
		% C	% H	
<i>I</i>	C ₁₉ H ₁₆ FeO (316.2)	72.18 72.10	5.10 5.00	133–135 (80)
<i>II</i>	C ₁₉ H ₁₅ ClFeO (350.6)	65.09 64.60	4.31 4.09	101–103 (93)
<i>III</i>	C ₁₉ H ₁₅ BrFeO (395.1)	57.76 57.92	3.83 3.74	95–97 (90)
<i>IV</i>	C ₂₂ H ₂₀ FeO (356.2)	74.17 74.20	5.66 5.85	134–136 (70)
<i>V</i>	C ₂₄ H ₂₄ FeO (384.3)	75.01 75.19	6.29 6.45	98–100 (60)
<i>VI</i>	C ₁₉ H ₁₆ RuO (361.4)	63.14 63.00	4.46 4.37	159–161 (82)
<i>VII</i>	C ₁₇ H ₁₁ MnO ₄ (334.2)	61.10 60.86	3.32 3.16	124–126 (56)
<i>VIII</i>	C ₂₉ H ₂₄ FeO ₂ (460.4)	75.66 75.23	5.25 4.96	116–118 (6.2)
<i>IX</i>	C ₃₁ H ₂₈ FeO ₂ (488.4)	76.24 75.83	5.78 6.06	136–139 (9.4)
<i>X</i>	C ₂₆ H ₂₀ FeO ₂ (420.3)	74.30 74.62	4.80 4.40	109–110 (14)
<i>XI</i>	C ₁₉ H ₁₅ ClFeO (350.6)	65.09 64.76	4.41 4.13	82–85 (47.5)

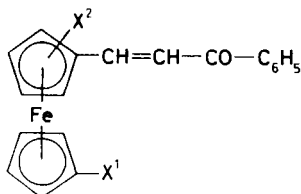
2-chloro and 2-bromoferrocenecarbaldehydes. The known method for preparation of 2-chloro and 2-bromoferrocenylmethylidimethylamine and 2-chloro and 2-bromoferrocenylmethanols⁶ was employed instead. The attempt to oxidize 2-bromoferrocenylmethanol and 2-bromoferrocenylmethylidimethylamine with active MnO_2 , or $BaMnO_4$ was accompanied with cleavage of bromine and the yield of ferrocenecarbaldehyde was very low (10%). On the other hand, only a partial cleavage of

TABLE II

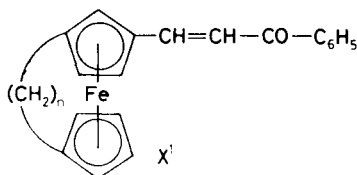
¹H NMR spectra of metallocene analogues of chalcones

Compound	Chemical shifts (δ , ppm) and coupling constants J (Hz)
<i>I</i>	7.95 (m, 2 H, C_6H_5), 7.53 (m, 2 H, C_6H_5), 7.76 (d, 1 H, $-CH=$), 7.14 (d, 1 H, $J = 16$ Hz, $-CO-CH=$), 4.60 (t, 2 H, H_α), 4.49 (t, 2 H, H_β), 4.18 (s, 5 H, C_5H_5)
<i>II</i>	7.98 (m, 2 H, C_6H_5), 7.51 (m, 3 H, C_6H_5), 7.69 (d, 1 H, $-CH=$), 7.17 (d, 1 H, $J = 15.5$ Hz, $-CO-CH=$), 4.63 (t, 2 H, H_α), 4.52 (t, 2 H, H_β), 4.38 (t, 2 H, H_α), 4.07 (t, 2 H, H_β)
<i>III</i>	8.00 (m, 2 H, C_6H_5), 7.54 (m, 3 H, C_6H_5), 7.70 (d, 1 H, $-CH=$), 7.17 (d, 1 H, $J = 15$ Hz, $-CO-CH=$), 4.61 (t, 2 H, H_α), 4.54 (t, 1 H, H_β), 4.38 (t, 2 H, H_α), 4.11 (t, 2 H, H_β)
<i>IV</i>	7.98 (m, 2 H, C_6H_5), 7.58–7.16 (m, 5 H, C_6H_5 and $-CH=CH-$), 3.80 (m, 7 H, C_5H_4 and C_5H_3), 1.90 (m, 6 H, $-CH_2-$)
<i>V</i>	7.96 (m, 2 H, C_6H_5), 7.54 (m, 3 H, C_6H_5), 7.76 (d, 1 H, $-CH=$), 7.09 (d, 1 H, $J = 15.6$ Hz, $-CO-CH=$), 4.55–3.25 (m, 7 H, C_5H_4 and C_5H_3), 2.53–1.70 (m, 10 H, $-CH_2-$)
<i>VI</i>	7.94 (m, 2 H, C_6H_5), 7.70 (m, 3 H, C_6H_5), 7.63 (d, 1 H, $-CH=$), 7.09 (d, 1 H, $J = 15.4$ Hz, $-CO-CH=$), 4.98 (t, 2 H, H_α), 4.75 (t, 2 H, H_β), 4.56 (s, 5 H, C_5H_5)
<i>VII</i>	7.94 (m, 2 H, C_6H_5), 7.55 (m, 3 H, C_6H_5), 7.28 (m, 2 H, C_6H_5 and $CH=CH$), 5.2 (t, 2 H, H_α), 4.85 (t, 2 H, H_β)
<i>VIII</i>	8.08–6.75 (m, 12 H, C_6H_5 and $-CH=CH-$), 4.63–3.30 (m, 6 H, C_5H_3), 1.86 (m, 6 H, $-CH_2-$)
<i>IX</i>	7.91–7.28 (m, 12 H, C_6H_5 and $-CH=CH-$), 4.33–3.33 (m, 6 H, C_5H_3), 1.94–1.45 (m, 10 H, $-CH_2-$)
<i>X</i>	7.50–7.82 (m, 10 H, C_6H_5), 7.81 (d, 1 H, $=CH-$), 7.00 (d, 1 H, $J = 15.5$ Hz, $-CO-CH=$), 4.87 (m, 2 H, H_α), 4.55 (m, 4 H, C_5H_4), 4.47 (m, 2 H, H_β)
<i>XI</i>	7.96 (m, 2 H, C_6H_5), 7.55 (m, 3 H, C_6H_5), 7.90 (d, 1 H, $-CH=$), 7.35 (d, 1 H, $J = 15$ Hz, $-CO-CH=$), 4.70 (m, 1 H, C_5H_3), 4.58 (m, 1 H, C_5H_3), 4.36 (m, 1 H, C_5H_3), 4.24 (s, 5 H, C_5H_5)

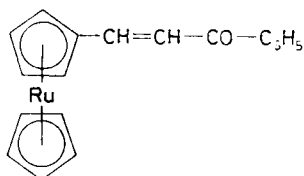
chlorine took place when oxidizing 2-chloroferrocenylmethanol and 2-chloroferrocenylmethyl dimethylamine. 2-Chloroferrocenecarbaldehyde was prepared in 12% yield by the analogous procedure with that described by Schlögl⁷.



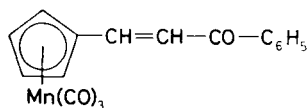
- I, $X^1 = X^2 = H$
 II, $X^1 = Cl$; $X^2 = H$
 III, $X^1 = Br$; $X^2 = H$
 X, $X^1 = COC_6H_5$; $X^2 = H$
 XI, $X^1 = H$; $X^2 = Cl$



- IV, $X^1 = H$; $n = 3$
 V, $X^1 = H$; $n = 5$
 VIII, $X^1 = COC_6H_5$; $n = 3$
 IX, $X^1 = COC_6H_5$; $n = 5$



VI



VII

Preliminary experiments with Michael addition of ethyl or methyl malonates to η^6 -benzenetricarbonylchromium analogues of chalcones² showed that the carbon atom is diastereotopic in the original malonate and thus, two individual signals were observed for hydrogens of ethyl or methyl groups $-\text{CH}(\text{COOCH}_3)_2$ in the ¹H NMR spectrum. Evidently, the chemical shift of one methyl can be influenced by the diamagnetic circular current of one of the chalcone aryl groups. This hypothesis was verified by products of Michael addition of methyl malonate to a series of different chalcone (Table III). The aryl group closer to $\text{CH}(\text{COOCH}_3)_2$ was predominantly changed, and the effect of the more remote aryl was tested with adducts XVI and XVII only. Considering the easiness of the course of electrophilic substitutions⁸, the π -electron density of the aryls under investigation should decrease in the series ferrocenyl > ruthenocenyl > $\eta^5\text{-C}_3\text{H}_4\text{Mn}(\text{CO})_3 \cong \text{phenyl} > \eta^6\text{-C}_6\text{H}_5\text{-Cr}(\text{CO})_3$. The measured data (Table IV) show that the quality of metalloocenyl is of no significant effect on the change of the chemical shift difference of the methyl group hydrogens. Contrast of $\Delta\delta$ CH_3 groups displayed a great effect of benzene circular currents on the chemical shift of the methyl groups (adducts XII and XVI):

Adduct	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
$\Delta\delta(\text{CH}_3)$, ppm	0.218	0.077	0.060	0.065	0.243	0	0.043	0.067

The methyl group $\text{C}=\text{CH}-\text{CH}_3$ of compound *XVI* does not influence the chemical shift of $-\text{COOCH}_3$ groups; they absorb as one singlet integrating 6 protons. Nevertheless, the $-\text{CH}-\text{CH}_3$ group signal was a doublet thus providing evidence for the presence of two diastereoisomers in the product.

TABLE III
Adducts of ethyl malonate to metallocene analogues of chalcones

$$\begin{array}{c} \text{CH}(\text{COOCH}_3)_2 \\ | \\ \text{R}^1-\text{CH}-\text{CH}_2-\text{CO}-\text{R}^2 \end{array}$$

Compound	R^1 R^2	Formula (M_r)	Calculated/found		M.p., °C (Yield, %)
			% C	% H	
<i>XII</i>	C_6H_5	$\text{C}_{20}\text{H}_{20}\text{O}_5$ (340.4)	70.57	5.92	104–106
	C_6H_5		70.45	5.93	(82)
<i>XIII</i>	Bct	$\text{C}_{23}\text{H}_{20}\text{CrO}_8$ (476.4)	57.99	4.23	128–130
	C_6H_5		57.87	4.08	(70)
<i>XIV</i>	2- CH_3 Bct	$\text{C}_{24}\text{H}_{22}\text{CrO}_8$ (490.4)	58.78	4.52	101–103
	C_6H_5		58.48	4.41	(75)
<i>XV</i>	Fc	$\text{C}_{24}\text{H}_{24}\text{FeO}_5$ (448.3)	64.30	5.39	139–141
	C_6H_5		64.73	5.48	(67)
<i>XVI</i>	C_6H_5	$\text{C}_{24}\text{H}_{24}\text{FeO}_5$ (448.3)	64.30	5.39	134–136
	Fc		64.38	5.50	(62)
<i>XVII</i>	CH_3	$\text{C}_{19}\text{H}_{22}\text{FeO}_5$ (386.2)	59.09	5.74	55–57
	Fc		59.46	5.86	(78)
<i>XVIII</i>	Rc	$\text{C}_{24}\text{H}_{24}\text{RuO}_5$ (493.5)	58.41	4.90	154–156
	C_6H_5		58.30	4.95	(46)
<i>XIX</i>	Cym	$\text{C}_{22}\text{H}_{19}\text{MnO}_8$ (466.3)	56.66	4.11	111–113
	C_6H_5		56.36	3.96	(52)

^a Bct η^6 -benzenetricarbonylchromium, Fc ferrocenyl, Rc ruthenocenyl, cym η^5 -cyclopentadienyltricarbonylmanganese.

EXPERIMENTAL

Ruthenocenecarbaldehyde was prepared in 58% yield according to⁹, cymanthrncarbaldehyde in 23% yield according to¹⁰ and ferrocenecarbaldehyde according to¹¹. [3] And [5]ferrocenophane-3-carbaldehydes were synthesized applying the Vilsmeire-Haack formylation¹², 1-ferrocenyl-3-phenylpropenone and crotonylferrocene were obtained according to¹³ and ¹⁴, respectively. 2-Chloro and 2-bromo(N,N-dimethylaminomethyl)ferrocenes were synthesized according to⁶. All experiments with the organometallic derivatives were carried out in a nitrogen atmosphere, the products were separated by column chromatography over silica gel or alumina, the eluent being benzene-ethyl acetate. The melting points were determined on a Kofler micro hot-stage, the ¹H NMR spectra were taken with a Tesla BS 487 A spectrometer operating at 80 MHz.

TABLE IV

¹H NMR spectra of adducts of methyl malonate to metallocene analogues of chalcones

Compound	Chemical shift (δ , ppm) and coupling constants J (Hz)
XII	7.88 mm, 2 H, C ₆ H ₅), 7.45 (m, 2 H, C ₆ H ₅), 7.36 (m, 6 H, C ₆ H ₅), 4.35—3.78 (m, 2 H, —CH—CH—), 3.72 (s, 3 H, COOCH ₃), 3.53 (m, 2 H, —CH ₂ —), 3.50 (s, 3 H, COOCH ₃)
XIII	7.99 (m, 2 H, C ₆ H ₅), 7.48 (m, 3 H, C ₆ H ₅), 5.84 (m, 2 H, C ₆ H ₅ —Cr), 5.41 (m, 3 H, C ₆ H ₅ —Cr), 3.91 (m, 4 H, >CH—CH—CH ₂ —), 3.59 (s, 3 H, COOCH ₃), 3.52 (s, 3 H, COOCH ₃)
XIV	8.06 (m, 2 H, C ₆ H ₅), 7.60—7.30 (m, 3 H, C ₆ H ₅), 5.69 (m, 1 H, C ₆ H ₅ —Cr), 5.45 (m, 1 H, C ₆ H ₅ —Cr), 5.01 (m, 2 H, C ₆ H ₅ —Cr), 4.16 (m, 1 H, —CH—), 3.89—3.66 (m, 3 H, —CH—CH ₂ —), 3.63 (s, 3 H, COOCH ₃), 3.56 (s, 3 H, COOCH ₃)
XV	8.05 (m, 2 H, C ₆ H ₅), 7.53 (m, 3 H, C ₆ H ₅), 4.11 (s, 10 H, C ₅ H ₅ , C ₅ H ₄ and >CH), 3.84 (m, 2 H, —CH ₂ —), 3.48 (m, 1 H, —CH—), 3.65 (s, 3 H, COOCH ₃), 3.57 (s, 3 H, COOCH ₃)
XVI	7.4 (m, 5 H, C ₆ H ₅), 4.70 (t, 2 H, H _{α}), 4.44 (t, 2 H, H _{β}), 4.44 (t, 2 H, H _{β}), 4.13 (m, 1 H, —CH—), 3.96 (s, 5 H, C ₅ H ₅), 3.84 (m, 1 H, —CH—), 3.74 (s, 3 H, COOCH ₃), 3.50 (s, 3 H, COOCH ₃), 3.2 (m, 2H, —CH ₂)
XVII	4.83 (t, 2 H, H _{α}), 4.50 (t, 2 H, H _{β}), 4.20 (s, 5 H, C ₅ H ₅), 3.75 (s, 6 H, COOCH ₃), 3.52 (m, 1 H, —CH<), 3.04—2.70 (m, 3 H, —CH—CH ₂ —), 1.17 (d, 3 H, —CH—CH ₃) and 1.09 (d, 3 H, —CH—CH ₃)
XVIII	7.99 (m, 2 H, C ₆ H ₅), 7.51 (m, 3 H, C ₆ H ₅), 4.64 (t, 2 H, H _{α}), 4.56 (t, 2 H, H _{β}), 4.46 (s, 5 H, C ₅ H ₅), 3.83 (m, 2 H, —CH ₂ —), 3.50 (m, 2 H, —CH—CH—), 3.68 (s, 3 H, COOCH ₃), 3.63 (s, 3 H, COOCH ₃)
XIX	8.00 (m, 2 H, C ₆ H ₅), 7.53 (m, 3 H, C ₆ H ₅), 5.20 (m, 2 H, H _{α}), and 5.05 (m, 2 H, H _{α}), 4.84 (m, 2 H, H _{β}), and 4.70 (m, 2 H, H _{β}), 3.85 (m, 4 H, —CH—CH—CH ₂), 3.63 (s, 3 H, COOCH ₃), 3.56 (s, 3 H, COOCH ₃)

Measured were C^2HCl_3 or $(C^2H_3)_2CO$ solutions and the chemical shifts values (δ , ppm) are relative to tetramethylsilane.

1'-Chloroferrocenecarbaldehyde

Chloroferrocene (4.4 g, 20 mmol) was added at room temperature to a stirred solution of N-methylformanilide (7.2 g, 52 mmol) and $POCl_3$ (5.1 g, 330 mmol). Stirring was continued for 1 h at an ambient temperature and at 65–70°C for additional 2 h. The mixture was cooled, sodium acetate (17 g) in water (133 ml) was added and the solution was stirred at room temperature overnight, poured into water, the organic material was taken into chloroform, the latter was washed with water, dried and evaporated. The residue was chromatographed over silicagel with benzene as eluent. The first band afforded a small amount of the starting material, the second band gave 1'-chloroferrocenecarbaldehyde (1.1 g, 24%), m.p. 43–46°C (hexane). For $C_{11}H_9FeClO$ (248.5) calculated: 53.16% C, 3.65% H, 22.55% Fe; found: 53.24% C, 3.71% H, 22.96% Fe. 1H NMR spectrum: 9.99 (s, 1 H, CHO), 4.84 (t, 2 H, H_α), 4.63 (t, 2 H, H_β), 4.48 (t, 2 H, H_α'), 4.15 (t, 2 H, H_β').

1'-Bromoferrocenecarbaldehyde

Applying the above-mentioned procedure and starting from N-methylformanilide (3.6 g, 17 mmol), $POCl_3$ (2.6 g, 17 mmol) and bromoferrocene (2.7 g, 10 mmol), 1'-bromoferrocenecarbaldehyde (1.2 g, 42%) was obtained m.p. 58–60°C (light petroleum). For $C_{11}H_9BrFeO$ (292.91) calculated: 45.15% C, 3.09% H, 19.06% Fe; found: 45.18% C, 3.20% H, 19.40% Fe. 1H NMR spectrum: 10.0 (s, 1 H, CHO), 4.80 (t, 2 H, H_α), 4.66 (t, 2 H, H_β), 4.58 (t, 2 H, H_α'), 4.26 (t, 2 H, H_β').

2-Chloroferrocenecarbaldehyde

Active MnO_2 (3.48 g, 40 mmol) was added to a stirred solution of 2-chloro(N,N-dimethylamino)methylferrocene in chloroform–benzene (40 ml, 1 : 1); stirring was continued for 24 h at room temperature and then the mixture was refluxed for 3 h. The solid was filtered off, the solvent was removed and the residue was chromatographed over alumina. Elution with benzene afforded 2-chloroferrocenecarbaldehyde (0.06 g, 12%), m.p. 87–90°C. For $C_{11}H_9FeClO$ (248.5) calculated: 53.17% C, 3.65% H; found: 53.26% C, 3.86% H. 1H NMR spectrum: 10.21 (s, 1 H, —CHO), 4.81 (m, 2 H, C_5H_3), 4.56 (m, 1 H, C_5H_3), 4.39 (s, 5 H, C_5H_5).

1-Phenyl-3-metallocenyl-2-propenones

Acetophenone (5 mmol) was added to a stirred solution of metallocenecarbaldehyde (5 mmol) in ethanol (95%, 10 ml). After a successive addition of aqueous–methanolic NaOH (5 mmol) the mixture was stirred for 3–4 h at room temperature, the precipitated product was filtered off, washed with water and crystallized from dilute methanol. Results of this reaction and elemental analyses are listed in Table II.

Benzoylation of Chalcones I, IV, and V

Anhydrous $AlCl_3$ (10 mmol) was successively added at 5–10°C to a stirred solution of the respective chalcone (6.6 mmol) and benzoyl chloride (6.6 mmol) in dichloromethane (80 ml). The mixture was stirred at room temperature for 4 h and then poured into ice-cold water (500 ml). The organic product was extracted with dichloromethane, the extract was washed with water and 5%- $NaHCO_3$, dried, the solvent was removed and the residue was chromatographed through

an alumina-packed column. Elution with benzene-ethyl acetate (9:1) stepwise afforded: Chalcone *I*, the starting material (57%) and 1,3-diphenyl-2-ferrocenylmethylene-1,3-propanedione (11%), m.p. 197–200°C (acetone-heptane). For $C_{26}H_{20}FeO_2$ (420.3) calculated: 74.30% C, 4.79% H, 13.29% Fe; found: 74.54% C, 4.81% H, 13.51% Fe. 1H NMR: 8.03–7.37 (m, 11 H, C_6H_5 and $=CH-$), 4.38 (t, 2 H, H_a), 4.30 (t, 2 H, H_b), 4.17 (s, 5 H, C_5H_3). The third chromatographic band gave compound *X* (cf. Tables I and II).

Chalcone *IV*: The first chromatographic band furnished the starting material (56%), the second band afforded 3-(3-benzoyl-3-phenyl-3-oxo-1-propenyl)[3]ferrocenophane (15.5%), m.p. 219 to 221°C (ether-light petroleum). For $C_{29}H_{24}FeO_2$ (460.3) calculated: 75.66% C; 5.25% H; found: 75.26% C; 4.83% H; 1H NMR spectrum: 8.01–7.23 (m, 11 H, C_6H_5 and $=CH-$); 6.65 (m, 4 H, C_5H_4); 6.50 (s, 1 H, C_5H_3); 6.33–5.75 (m, 2 H, C_5H_3); 1.63 (m, 6 H, $-CH_2-$).

Chalcone *V*: The first chromatographic band furnished the starting material (20%), the second band afforded 3-(2-benzoyl-3-phenyl-3-oxo-1-propenyl)[5]ferrocenophane (23.6%), m.p. 164 to 166°C (benzene-light petroleum). For $C_{31}H_{28}FeO_2$ (488.4) calculated: 76.22% C, 5.78% H; found: 75.96% C, 6.08% H. 1H NMR spectrum: 8.08–7.38 (m, 11 H, C_6H_5 and $=C-$), 4.24 (t, 2 H, H_a), 4.13 (t, 2 H, H_b), 3.88–3.25 (m, 3 H, C_5H_3), 2.4–1.58 (m, 10 H, $-CH_2-$). Compound *IX* (cf. Tables I and II) was obtained from the third band.

Addition of Methyl Malonate to the Metallocene Analogues of Chalcones

An equimolar amount of methyl malonate was added to the stirred solution of the metallocene analogue of chalcone (2.5 mmol) in ether (25 ml). Sodium methoxide (1 mol l^{-1} solution, 25 mmol) was added dropwise and the mixture was stirred at an ambient temperature. The reaction course was monitored by thin-layer chromatography: the reaction time for $C_6H_5Cr(CO)_3$ analogues of chalcones was 5–8 min, that for ferrocene analogues of chalcones up to 24 h. After that the mixture was poured into water, the product was extracted and dried, the solvent was distilled off and the residue was either crystallized from ethanol-water (compounds *XII*, *XIII*, *XVI*–*XIX*), or chromatographically purified and crystallized (compounds *XIV*, *XV*). Results and analyses are presented in Table III, the 1H NMR spectral data are listed in Table IV.

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