Journal of Organometallic Chemistry, 338 (1988) 211–216
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

η^6-Benzenetricarbonylchromium analogues of chalcones

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(Received June 17th, 1987)

Abstract

Synthesis of 11 η^6-benzenetricarbonylchromium analogues of chalcones, starting from the appropriately substituted η^6-benzaldehydetricarbonylchromium as well as substituted η^6-acetophenonetricarbonylchromium complexes is described.

Dimethylmalonate addition to the chalcone and its $Cr(CO)_3$ complex takes place with the same regioselectivity.

The effect of complexation of a benzene moiety with tricarbonylchromium is well known and is described in several reviews [1–4]. The most prominent feature of benzene complexation with $Cr(CO)_3$ group is the facility for nucleophilic attack and the direction of a nucleophile or a base from the *anti* position to the $Cr(CO)_3$ group. This directing effect is ascribed to the bulkiness of the $Cr(CO)_3$ group [5,6] but there is only one report [7] describing such a directing effect to a group other than carbonyl group.

Several η^6-benzenetricarbonylchromium analogues of chalcones have been synthesized [8,9] but neither their spectral characteristics nor reactivity (except polarographic reduction) were studied. Several substituted benzaldehydetricarbonylchromium complexes have been described [8–10] but their spectral characteristics were absent.

The main goal of this work was to synthesize several properly substituted η^6-benzenetricarbonylchromium analogues of chalcones, as the starting materials for intended stereochemical studies of the Michael addition.

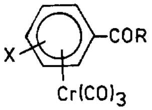
Results and discussion

The synthesis of η^6-benzenetricarbonylchromium analogues of chalcones from the appropriately substituted benzaldehydes or acetophenones. The synthesis of

0022-328X/88/$03.50

Table 1

Substituted η^6-benzaldehyde- and acetophenonetricarbonylchromium complexes [a]

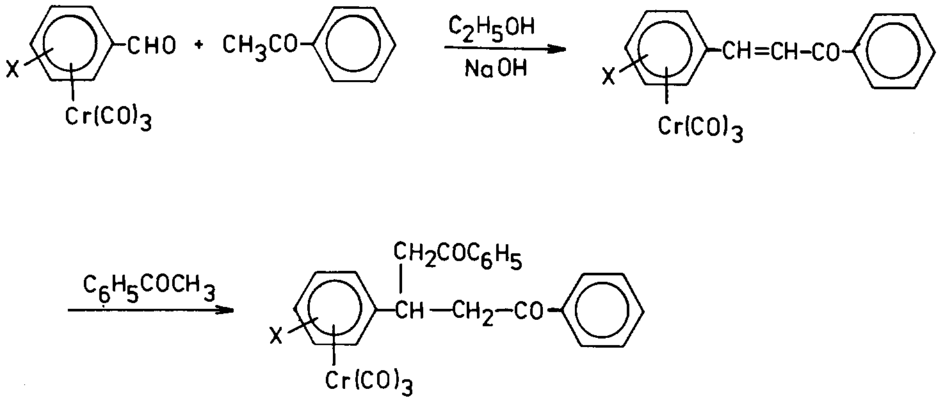


R	X	Yield (%)	M.p. (°C) M.p. [Ref.]	^{1}H NMR		
				R	C_6H_4	X
H	H	90	44–46 78.5 [15]	9.43(s,1H)	5.93(m,2H) 5.69(t,1H) 5.26(m,2H)	
H	2-CH_3	87	78–80 75 [8]	9.79(s,1H)	6.04(d,1H) 5.73(t,1H) 5.31(t,1H) 5.04(d,1H)	2.53(s,3H)
H	3-CH_3	40	oil 47 [8]	9.50(s,1H)	5.80(s,1H) 5.63–5.05(m,3H)	2.53(s,1H)
H	2-OCH_3	50	88–90 90 [10]	10.03(s,1H)	6.21(d,1H) 5.85(t,1H) 5.03(m,2H)	3.86(s,3H)
H	3-OCH_3	40	oil 62–63 [8]	9.86(s,1H)	6.16(m,1H) 5.78–5.26(m,3H)	3.65(s,3H)
H	2-Cl	10	51–53 71 [8]	9.65(s,1H)	5.92(m,1H) 5.76–5.28(m,3H)	
H	3-Cl	6	oil –	9.56(s,1H)	5.96(m,1H) 5.81–5.32(m,3H)	
CH_3	H	30	83–85 85 [8]	2.46(s,3H)	6.05(d,2H) 5.64(t,1H) 5.28(m,2H)	
CH_3	2-CH_3	50	59–61	2.46(s,3H)	5.94(d,1H) 5.65(t,1H) 5.14(m,2H)	2.54(s,3H)

[a] The purity of all compounds was checked by TLC and elemental analysis.

dimethylacetals of these carbonyl compounds by Taylor's procedure [11] caused no problems. The complexation of acetals with $Cr(CO)_6$ by Pauson's method [12] went smoothly; the only exception was complexation of acetals derived from 2-, and 3-chlorobenzaldehydes. With these acetals overall decomposition of the material was observed during complexation and also during HCl/H_2O hydrolysis of the complexed acetals to give the corresponding η^6-chlorobenzaldehydetricarbonylchromium complexes. This is shown by their very low yields (Table 1). Recently [13] we found that hydrolysis of the complexed dimethylacetals as well as dioxolanes of aromatic aldehydes with phosphoric acid proceeds smoothly and without decomposition.

The condensation of substituted η^6-benzaldehydetricarbonylchromium complexes with acetophenone went smoothly, with high yields. The reaction in some cases was



Scheme 1

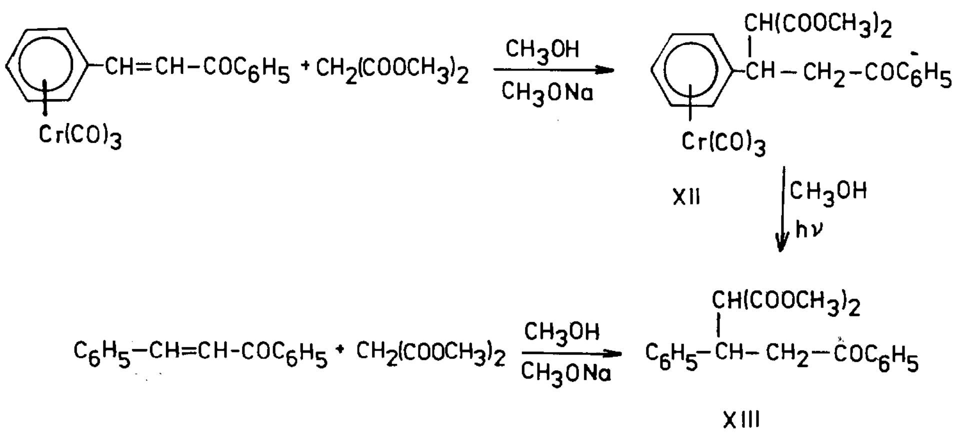
complicated by Michael addition of acetophenone to the formed condensation product (Scheme 1).

The acetophenone adducts were isolated in the cases when:

X = *2-CH$_3$*, m.p. 134–136 °C. Found: C, 68.08; H, 4.68. $C_{27}H_{22}CrO_5$ (487.47) calc: C, 67.80; H, 4.64%. ^{1}H-NMR spektrum (δ (ppm)): 7.94 (m, 4H, C_6H_5); 7.46 (m, 6H, C_6H_5); 6.03 (d, 1H, C_6H_5-Cr); 5.59 (t, 1H, C_6H_5-Cr); 5.24 (m, 2H, C_6H_5-Cr); 3.90 (m, 1H, CH); 3.75–3.20 (m, 4H, CH_2); 2.31 (s, 3H, CH_3).

X = *2-Cl*, m.p. 149–150 °C. Found: C, 62.08; H, 3.82; Cl, 6.60. $C_{26}H_{19}ClCrO_5$ (498.89) calc: C, 62.12; H, 3.78; Cl, 7.05%. ^{1}H-NMR spectrum (δ (ppm)): 8.13–7.78 (m, 4H, C_6H_5), 7.56–7.40 (m, 6H, C_6H_5); 6.21 (d, 1H, C_6H_5-Cr); 5.88–5.60 (m, 2H, C_6H_5-Cr); 5.30 (m, 1H, C_6H_5-Cr); 3.84 (m, 1H, CH); 3.73–3.38 (m, 4H, CH_2).

To prove that the regioselectivity of the addition of dimethylmalonate to complexed or to free chalcone is the same, photolytic decomposition of the complexed compound XII was carried out. The melting point, TLC and ^{1}H NMR data of the product XIII were identical with those of the product prepared in the conventional way (Scheme 2).



XII

XIII

Scheme 2

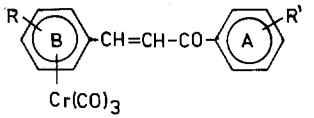
Experimental

The ^1H NMR spectra were recorded at 25 °C on a Tesla Brno BS 487 instrument at 80 MHz. The spectra were recorded in $(C^2H_3)_2CO$ solutions with tetramethylsilane as internal standard. IR spectra were recorded on a Perkin–Elmer 180 instrument. Melting points were recorded on a Kofler apparatus and are uncorrected. All of the syntheses were carried out under purified nitrogen.

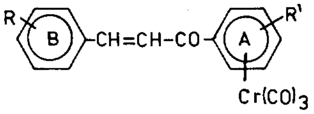
The dimethylacetals of the appropriately substituted benzaldehydes or acetophenones [15] were complexed as described by Pauson [12] and the hydrolysis of the acetals to the substituted benzaldehyde or acetophenonetricarbonylchromium complexes by procedures described by Drefahl and Rausch [16,17]. The yields, physical constants and ^1H NMR data of the prepared complexes are listed in Table 1.

Table 2

Physical constants and IR spectra of η^6-benzenetricarbonylchromium chalcone analogues



I – VIII



IX– XI

Compound	R	Formula (M)	Analysis (Found (calc) (%))			M.p. (°C) Yield (%)	IR	
			C	H	Cl		ν(C=O)	ν(C=O) ν(C=C)
I	H	$C_{18}H_{12}CrO_4$	62.82	3.57		145–150	1970, 1900	1680
		(344.29)	(62.79)	(3:51)		60		1600
II	2-CH_3	$C_{19}H_{14}CrO_4$	63.78	3.76		99–101	1970, 1880	1670
		(358.32)	(63.69)	(3.94)		85		1590
III	3-CH_3	$C_{19}H_{14}CrO_4$	63.61	3.83		124–126	1970, 1880	1660
		(358.32)	(63.69)	(3.94)		70		1600
IV	2-OCH_3	$C_{19}H_{14}CrO_5$	60.96	3.73		129–131	1950, 1840	1660
		(374.32)	(60.97)	(3.77)		65		1590
V	3-OCH_3	$C_{19}H_{14}CrO_5$	61.35	3.84		130–132	1960, 1870	1660
		(374.32)	(60.97)	(3.77)		72		1600
VI	2-Cl	$C_{18}H_{11}ClCrO_4$	57.32	3.35	9.20	141–143	1970, 1900	1660
		(378.74)	(57.08)	(2.93)	(9.36)	30		1580
VII	3-Cl	$C_{18}H_{11}ClCrO_4$	57.36	2.89	9.17	124–126	1960, 1910	1660
		(378.74)	(57.08)	(2.93)	(9.36)	15		1590
VIII	2′-CH_3	$C_{19}H_{14}CrO_4$	63.26	4.00		163–165	1960, 1860	1640
		(358.32)	(63.69)	(3.94)		70		1610
IX	H	$C_{18}H_{12}CrO_4$	62.93	3.52		123–125	1980, 1880	1650
		(344.29)	(62.79)	(3.51)		52		1600
X	2-CH_3	$C_{19}H_{14}CrO_4$	63.29	3.89		125–127	1970, 1880	1650
		(358.32)	(63.69)	(3.94)		60		1590
XI	2′-CH_3	$C_{19}H_{14}CrO_4$	63.76	3.93		80– 82	1970, 1900	1660
		(358.32)	(63.69)	(3.94)		80		1600

Synthesis of η^6-benzenetricarbonylchromium analogues of chalcones

To a stirred solution of 1 mmol of the appropriately substituted η^6-benzaldehydetricarbonylchromium complex in 10 ml of ethanol was added 1 mmol of acetophenone and then 1 mmol of NaOH in a 50% ethanol/water (1/1) solution. Separation of the η^6-benzenetricarbonylchromium chalcone analogue began after

Table 3

^{1}H NMR spectra (δ (ppm); J (Hz)) of η^6-benzenetricarbonylchromium chalcone analogues

Compound	R'-C_6H_4 (A)	-CH= =CH-CO- J_{AB}	R-C_6H_4 (B)	R
I	8.03(m,2H) 7.50(m,3H)	7.69(d,1H) 7.31(d,1H) 16	6.13(m,2H) 5.65(m,3H)	–
II	8.01(d,2H) 7.60–7.43(m,3H)	7.69(d,1H) 7.37(d,1H) 16	6.59(d,1H) 5.57(d,1H) 5.27(t,1H) 5.20(d,1H)	2.39(s,3H)
III	8.03(m,2H) 7.53(m,3H)	7.70(d,1H) 7.33(d,1H) 16	6.04–5.43(m,3H)	2.20(s,3H)
IV	8.00(d,2H) 7.66–7.43(m,3H)	7.81(d,1H) 7.40(d,1H) 15.7	6.03(d,1H) 5.71(t,1H) 5.15(d,1H) 5.01(t,1H)	3.86(s,3H)
V	8.03(m,2H) 7.51(m,3H)	7.71(d,1H) 7.39(d,1H) 16	5.87(m,2H) 5.50(m,2H)	3.75(s,3H)
VI	8.02(d,2H) 7.69–7.48(m,3H)	7.93(d,1H) 7.40(d,1H) 15.7	5.94(d,1H) 5.18(t,1H) 5.46–5.30(m,2H)	–
VII	8.05(m,2H) 7.53(m,3H)	7.83(d,1H) 7.37(d,1H) 16	6.38(m,1H) 5.85(m,3H)	–
VIII	7.58(d,1H) 7.41(t,1H) 7.31(d,2H)	7.28(d,1H) 7.15(d,1H) 15.5	6.16(d,1H) 6.13(d,1H) 5.81(t,1H) 5.73(t,1H)	2.42(s,3H)
IX	7.58(m,2H) 7.44(m,2H)	7.89(d,1H) 7.16(d,1H) 16	6.15(d,2H) 5.63(m,1H) 5.29(t,2H)	–
X	7.76(m,1H) 7.48(m,1H) 7.23(m,2H)	8.05(d,1H) 7.20(d,1H) 16	6.44(d,2H) 5.90(m,1H) 5.55(t,2H)	2.40(s,3H)
XI	7.63(m,2H) 7.44(m,2H)	8.81(d,1H) 7.23(d,1H) 15.5	5.92(d,1H) 5.65(t,1H) 5.20(t,1H) 5.11(d,1H)	2.40(s,3H)

5–15 min of stirring. The reaction mixture was stirred at room temperature for a further 1–4 h. The crystals were filtered off, washed with water and recrystallized from ethanol.

The results and physical constants of the prepared compounds are listed in Table 2 and their spectral data in Table 3.

Michael additon of dimethylmalonate to 1-phenyl-3-(η^6-phenyltricarbonylchromium)-1-propenone

Dimethylmalonate (1.32 g, 10 mmol) and 1-phenyl-3-(η^6-phenyltricarbonylchromium)-1-propenone (0.35 g, 1 mmol) were dissolved in 20 ml of anhydrous diethyl ether. To the stirred reaction mixture was added 10 mmol of sodium methoxide solution in methanol (10% w.w) at room temperature. Aftėr stirring for 10 min the reaction mixture was washed with water and the ethereal solution was dried over anhydrous Na_2SO_4. After the solvent had been evaporated off the residue was recrystallized from a methanol/water mixture to yield yellow crystals of dimethyl 1-(η^6-phenyltricarbonylchromium)-3-phenyl-3-oxopropylmalonate (0.33 g, 70%) m.p. 128–130 °C. Found: C, 57.87; H, 4.08%. $C_{23}H_{20}CrO_8$ (476.41) calc: C, 57.99; H, 4.20%. ^1H NMR spectrum (δ) (ppm)): 7.99 (m, 2H, C_6H_5); 7.48 (m, 3H, C_6H_5); 5.84 (m, 2H, C_6H_5-Cr); 5.41 (m, 3H, C_6H_5-Cr); 3.91 (m, 4H, CH–CH–CH_2); 3.59 (s, 3H, $COOCH_3$); 3.52 (s, 3H, $COOCH_3$).

Michael additon of dimethylmalonate to the chalcone

The reaction was carried out as described above. After 24 h stirring at room temperature 0.20 g (58%) of dimethyl (1,3-diphenyl-3-oxopropyl)malonate, m.p. 104–106 ° C (methanol/water) was isolated from 0.49 (2 mmol) of chalcone. Found: C, 70.45; H, 5.93. $C_{20}H_{20}O_5$ (340.38) calc: C, 70.57; H, 5.92%. ^1H NMR spectrum (δ (ppm)): 7.88 (m, 2H, C_6H_5); 7.45 (m, 2H, C_6H_5); 7.36 (m, 6H, C_6H_5); 4.35–3.78 (m, 2H, -CH–CH-); 3.72 (s, 3H, $COOCH_3$); 3.53 (m, 2H, -CH_2); 3.50 (s, 3H, $COOCH_3$).

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