REGIOSELECTIVITY OF COMPLEXATIONS OF SUBSTITUTED PHENYL BENZOATES AND PHENYL PHENYLACETATES WITH $Cr(CO)_6$

Pavol HRNCIAR, Peter CERNAK, Vladimir GAJDA and Stefan TOMA

Department of Organic Chemistry,
Comenius University, 842 15 Bratislava, The Slovak Republic

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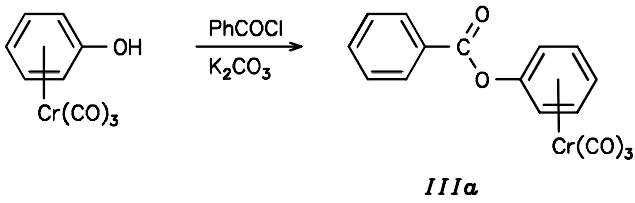
Selectivity of complexation of substituted phenyl benzoates is very low. In most cases, comparable yields of both regioisomeric complexes are isolated. Exception is 4-chlorophenyl ester, where benzoic acid moiety is complexed nearly exclusively. Very high regioselectivity of complexation was observed with substituted phenyl phenylacetates. The substituent of substituted phenols has not any effect on the complexation, and only phenylacetic acid moiety is complexed. This observation supports the recently proposed mechanism of the catalytic activity of the esters at arene complexation.

In our previous work[1] a regioselectivity of complexation of substituted 3-benzylidenephthalide has been studied. It was found that the complexation is directed by the substituent, which was characterized by the molecular electrostatic potential in the middle of both aromatic moieties present in the free ligand. It was of interest therefore to check if similar regioselectivity would be observed in other cases, too. In the present work substituted phenyl esters of benzoic and phenylacetic acids were chosen as model compounds for such a study.

The starting phenyl esters of benzoic as well as phenylacetic acids were prepared by standard method starting from acid chlorides and phenols[2]. The complexation of the esters was carried out with $Cr(CO)_6$ in boiling decalin, as described earlier[3]. The course of the complexation of phenyl benzoates is depicted in Scheme 1, and the results are given in Table I.

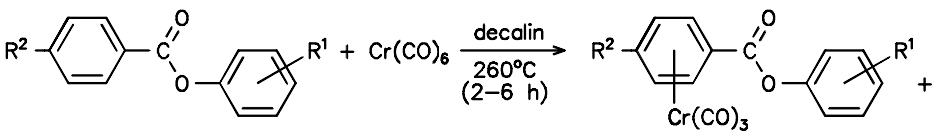
The structure assignment of complexation products of phenyl benzoates was straightforward from their ^1H NMR spectra as it was easy to see whether the chemical shifts of benzoic acid or phenol residue were shifted to the higher field due to the complexation with $Cr(CO)_3$ (see Experimental). The colour of the complexes or that of their solutions was very indicative, too. The complexes in which benzoic acid residue was complexed gave red solutions while those having complexed phenol moiety gave yellow solutions. This was expressed also in their UV-VIS spectra (the λ values are given in Scheme 1). To get an additional proof to this assignment, (η^6-phenyl)tricarbonylchromium benzoate was prepared via acylation of (η^6-phenol)tricarbonylchromium with benzoyl

chloride (Eq. (*A*)), and ^{1}H NMR as well as UV-VIS spectra of the products of both routes were compared.

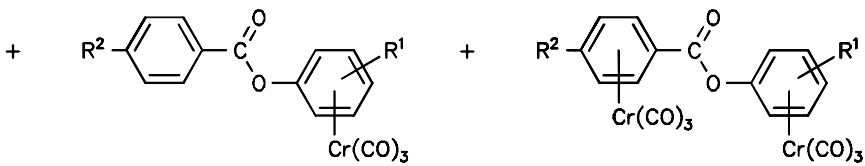


(*A*)

IIIa



I *II*



III *IVa, IVf*

In formulae *I–IV:*

	R^1	R^2
a	H	H
b	4-CH_3	H
c	2-CH_3	H
d	3-CH_3	H
e	3,4-$(CH_3)_2$	H
f	2,6-$(CH_3)_2$	H
g	4-Cl	H
h	H	4-Cl

λ_{max}, nm (ε, m^{-2} mol^{-1}):
IIa: 318 (3.23); 394 (2.55)
IIIa: 316 (3.026)
IVa: 320 (2.97); 398 (2.34)

SCHEME 1

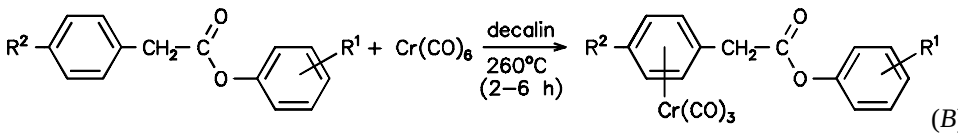
TABLE I
Products of complexation of substituted phenyl benzoates (Scheme 1)

Compound	M.p.,°C Yield, %	Formula (M.w.)	Calculated/Found	
			% C	% H
IIa	99.5 – 102	$C_{16}H_{10}CrO_5$	57.49	3.01
	33	(334.3)	57.53	3.01
IIIa	129.5 – 131	$C_{16}H_{10}CrO_5$	57.49	3.01
	18	(334.3)	57.44	2.90
IVa	>150 dec.	$C_{19}H_{10}CrO_8$	48.52	2.14
	13	(470.3)	48.75	2.16
IIb	87 – 89	$C_{17}H_{12}CrO_5$	58.62	3.47
	9	(348.3)	59.10	3.54
IIIb	125 – 128	$C_{17}H_{12}CrO_5$	58.62	3.47
	28	(348.3)	58.20	3.34
IIc	106 – 107	$C_{17}H_{12}CrO_5$	58.62	3.47
	12.5	(348.3)	59.02	3.82
IIIc	132 – 135	$C_{17}H_{12}CrO_5$	58.62	3.47
	32	(348.3)	57.16	3.23
IId	89 – 91	$C_{17}H_{12}CrO_5$	58.62	3.47
	7	(348.3)	58.14	3.23
IIId	128 – 131	$C_{17}H_{12}CrO_5$	58.62	3.47
	19	(348.3)	59.04	3.56
IIe	124 – 125.5	$C_{18}H_{14}CrO_5$	59.72	3.89
	4.7	(362.3)	60.03	3.52
IIIe	70 – 72	$C_{18}H_{14}CrO_5$	59.72	3.89
	31.6	(362.3)	59.05	3.20
IIf	93.5 – 95	$C_{18}H_{14}CrO_5$	59.72	3.89
	28	(362.3)	59.30	3.87
IIIf	119.5 – 121.5	$C_{18}H_{14}CrO_5$	59.72	3.89
	40.2	(362.3)	59.10	3.28
IVf	>149 dec.	$C_{21}H_{14}Cr_2O_8$	52.20	2.83
	5	(498.3)	52.10	2.91
IIg	116.5 – 117.5	$C_{16}H_9ClCrO_5$	52.12	2.46
	13.6	(368.7)	51.87	2.44
IIIh	135 – 136.5	$C_{16}H_9ClCrO_5$	52.12	2.46
	23	(368.7)	51.83	2.45

From the results given in Table I it follows that there is practically no regioselectivity of complexation of different phenyl benzoates. Only in the case of chloro substituted derivatives, the benzene ring not bearing chlorine was attacked predominantly at complexation of *Ig* (R^2 = H, R^1 = Cl), and a product of the reductive dehalogenation (*IIId*) was isolated, too. In these cases there are practically two electron-withdrawing groups (Cl–, –OCOR or Cl–, –COOR) on the same ring. This observation is in accord with the results of 3-benzylidenephthalide complexation[1].

It is of interest to mention that the main product of the complexation of unsubstituted phenyl benzoate is the product of benzoic acid moiety complexation, in spite of the fact that molecular electrostatic potential calculated by AM1 method[4,5] is more negative on the phenol moiety (–1.76 eV) than on the benzoic acid one (–1.511 eV). The complexation of benzoic acid moiety was observed even when the phenol moiety was substituted by one or two electron-donating methyl groups. This points to some autocatalytic or directing effect of the ester functionality (C=O bond).

The course of the complexation of substituted phenylacetates *V* is depicted in Eq. (*B*), and the results are given in Table II.

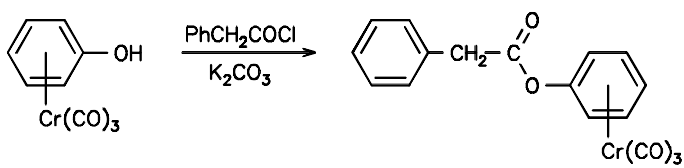


(*B*)

Va–Vg *VIa–VIg*

For R^1 and R^2 see Scheme 1

The structure assignment of the complexation products of phenyl phenylacetates was not so straightforward especially for the unsubstituted and some methyl substituted derivatives, as both aromatic moieties form just a broad singlet or multiplet in NMR spectra of the free ligand. For the above mentioned reason, (η^6-phenyl)tricarbonylchromium phenylacetate was prepared by an independent route (Eq. (*C*)).



(*C*)

VII

The chemical shift of the $-CH_2-$ group of this compound was found at 3.79 ppm, while the same chemical shift of the free ligand *IVa* was found at 3.83 ppm, and the product of complexation of *Va* has the chemical shift of the $-CH_2-$ group at 3.61 ppm.

A very characteristic feature of the ^{1}H NMR spectra of the complexation product of *Va* is a broad singlet of $C_6H_5Cr(CO)_3$ group at 5.37 ppm. Inspection of the NMR spectra of all complexation products (see Table III) reveals that the chemical shift of $-CH_2-$ group is located around 3.60 ppm, and all of them have a broad singlet for $C_6H_5Cr(CO)_3$ around 5.37 ppm. That means that in all cases the complexation took place on the phenylacetic acid moiety, in spite of the fact that calculated molecular electrostatic potential is nearly equal at $C_6H_5CH_2-$ (–1.927 eV) and C_6H_5O- (–1.881 eV) moiety.

These results document that the ester CO groups have a directing effect upon the complexation. It seems reasonable to propose that the first step of complexation is formation of the $>C=O \rightarrow Cr(CO)_5$ intermediate, and the $Cr(CO)_3$ group is then "ushered" underneath the appropriate benzene ring. This is in accord with the proposed catalytic effect of the esters at the complexations of arenes with $Cr(CO)_6$ (ref.[6]).

TABLE II
Products of complexation of substituted phenyl phenylacetates (Eq. (*B*))

Compound	M.p.,°C Yield, %	Formula (M.w.)	Calculated/Found	
			% C	% H
VIa	87 – 88.5	$C_{17}H_{12}CrO_5$	58.62	3.47
	47	(348.3)	58.48	3.38
VIb	107 – 108	$C_{18}H_{14}CrO_5$	59.67	3.89
	30	(362.3)	60.03	3.37
VIc	112 – 114	$C_{18}H_{14}CrO_5$	59.67	3.89
	32	(362.3)	59.28	3.49
VId	111	$C_{18}H_{14}CrO_5$	59.67	3.89
	24	(362.3)	59.34	3.52
VIe	86.5 – 88	$C_{19}H_{16}CrO_5$	60.64	4.28
	48	(376.3)	59.95	4.14
VIf	105.5 – 107.5	$C_{19}H_{14}CrO_6$	58.46	3.61
	45	(390.3)	58.83	3.56
VIg	103 – 105.5	$C_{17}H_{11}ClCrO_5$	53.40	2.89
	14.6	(382.7)	54.10	3.20
VII[a]	96 – 97.5	$C_{17}H_{12}ClCrO_5$	58.62	3.47
	14.5	(348.3)	58.67	3.42

[a] Equation (*C*).

TABLE III
^{1}H NMR spectra of new compounds

Compound	No.	^{1}H NMR spectrum ($CDCl_3$; δ, ppm; *J*, Hz)
Phenyl (η^6-benzoate)tricarbonyl-chromium	*IIa*	5.00 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.55 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 6.25 d, 2 H (*o*-$C_6H_5Cr(CO)_3$); 7.37 m, 5 H (Ph)
(η^6-Phenyl)tricarbonylchromium benzoate	*IIIa*	5.00 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.42 m, 3 H (*o,p*-$C_6H_5Cr(CO)_3$); 7.5 m, 3 H (*o,p*-$C_6H_5Cr(CO)_3$); 8.12 bd, 2 H (*m*-Ph)
(η^6-Phenyl)tricarbonylchromium (η^6-benzoate)tricarbonylchromium	*IVa*	5.00 t, 1 H; 5.40 m, 7 H; 6.17 d, 2 H
p-Tolyl (η^6-methylbenzoate)-tricarbonylchromium	*IIb*	2.37 s, 3 H (CH_3); 5.42 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.55 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 6.22 d, 2 H (*o*-$C_6H_5Cr(CO)_3$); 7.07 d, 2 H, *J*(A,B) = 6 (C_6H_4); 7.20 d, 2 H, *J*(A,B) = 6(C_6H_4)
(η^6-*p*-Tolyl)tricarbonylchromium benzoate	*IIIb*	2.14 s, 3 H (CH_3); 5.35 d, 2 H ($C_6H_4Cr(CO)_3$); 5.55 d, 2 H ($C_6H_4Cr(CO)_3$); 7.57 m, 3 H (*p*-Ph); 8.05 d, 2 H (*o*-Ph)
p-Tolyl (η^6-benzoate)-tricarbonylchromium	*IIc*	2.18 s, 3 H (CH_3); 5.07 t, 1 H ($C_6H_4Cr(CO)_3$); 5.28 d, 2 H ($C_6H_4Cr(CO)_3$); 5.50 d, 2 H ($C_6H_4Cr(CO)_3$); 7.82 m, 3 H (Ph); 8.40 d, 2 H (Ph)
(η^6-*o*-Tolyl)tricarbonylchromium benzoate	*IIIc*	2.26 s, 3 H (CH_3); 5.25 t, 2 H (*m*-$C_6H_4Cr(CO)_3$); 5.62 t, 1 H (*p*-$C_6H_4Cr(CO)_3$); 6.25 d, 2 H (*o*-$C_6H_4Cr(CO)_3$); 7.21 m, 4 H (C_6H_4)
m-Tolyl (η^6-benzoate)-tricarbonylchromium	*IId*	2.29 s, 3 H (CH_3); 4.89 d, 1 H, *J*(A,B) = 6 (C_6H_4); 5.94 bs, 2 H ($C_6H_4Cr(CO)_3$); 5.77 t, 1 H ($C_6H_4Cr(CO)_3$); 7.57 m, 3 H (*o,p*-Ph); 8.15 d, 2 H (*m*-Ph)
(η^6-*m*-Tolyl)tricarbonylchromium benzoate	*IIId*	2.38 s, 3 H (CH_3); 5.32 t, 2 H (*m*-$C_6H_4Cr(CO)_3$); 5.58 t, 1 H (*p*-$C_6H_4Cr(CO)_3$); 6.24 d, 2 H (*o*-$C_6H_4Cr(CO)_3$); 7.12 m, 4 H (C_6H_4)
3,4-Dimethylphenyl (η^6-benzoate)-tricarbonylchromium	*IIe*	2.11 s, 3 H (CH_3); 2.28 s, 3 H (CH_3); 5.47 m, 4 H (*m*-$C_6H_4Cr(CO)_3$); 7.58 m, 3 H (*m,p*-Ph); 8.13 d, 2 H (*o*-Ph)
(η^6-3,4-Dimethylphenyl)tricarbonyl-chromium benzoate	*IIIe*	2.27 s, 6 H (CH_3); 5.31 t, 2 H (*m*-$C_6H_4Cr(CO)_3$); 5.59 t, 1 H (*p*-$C_6H_4Cr(CO)_3$); 6.23 d, 2 H (*o*-$C_6H_4Cr(CO)_3$); 6.94 d, 2 H (C_6H_3); 7.11 s, 1 H (C_6H_3)
2,6-Dimethylphenyl (η^6-benzoate)-tricarbonylchromium	*IIf*	2.12 s, 3 H (CH_3); 2.22 s, 3 H (CH_3); 4.95 d, 1 H ($C_6H_3Cr(CO)_3$); 5.47 t, 2 H ($C_6H_4Cr(CO)_3$); 7.62 m, 3 H (Ph); 8.20 d, 2 H (Ph)
(η^6-2,6-Dimethylphenyl)tricarbonyl-chromium benzoate	*IIIf*	2.20 s, 3 H (CH_3); 2.32 s, 3 H (CH_3); 5.27 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.65 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 6.30 d, 2 H (*o*-$C_6H_5Cr(CO)_3$); 7.00 t, 3 H (C_6H_3)

TABLE III
(*Continued*)

Compound	No.	^{1}H NMR spectrum ($CDCl_3$; δ, ppm; *J*, Hz)
(η^6-2,6-Dimethylphenyl)tricarbonylchromium (η^6-benzoate)-tricarbonylchromium	*IVf*	2.15 s, 3 H (CH_3); 2.20 s, 3 H (CH_3); 4.95 d, 1 H ($C_6H_3Cr(CO)_3$); 5.30 t, 2 H ($C_6H_3Cr(CO)_3$); 5.45 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.70 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 6.25 d, 2 H (*o*-$C_6H_5Cr(CO)_3$)
4-Chlorophenyl (η^6-benzoate)-tricarbonylchromium	*IIg*	5.50 d, 2 H, *J*(A,B) = 2 (($C_6H_4ClCr(CO)_3$); 5.65 d, 3 H, *J*(A,B) = 3 ($C_6H_4ClCr(CO)_3$); 7.57 m, 3 H (Ph); 8.12 d, 2 H (Ph)
(η^6-4-Chlorophenyl)tricarbonylchromium benzoate	*IIIg*	5.30 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.62 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 7.10 d, 2 H, *J*(A,B) = 8 (C_6H_4Cl); 7.40 d, 2 H, *J*(A,B) = 8 (C_6H_4Cl)
(η^6-Phenyl)tricarbonylchromium 4-chlorobenzoate	*IIIh*	5.00 bt, 1 H (*p*-$C_6H_5Cr(CO)_3$); 5.50 m, 4 H ($C_6H_5Cr(CO)_3$); 7.53 d, 2 H (C_6H_4Cl); 8.03 d, 2 H (C_6H_4Cl)
Phenyl (η^6-phenylacetate)-tricarbonylchromium	*Va*	3.61 s, 2 H (CH_2); 5.37 m, 5 H ($C_6H_5Cr(CO)_3$); 7.07 dd, 2 H (*o*-Ph); 7.32 m, 3 H (Ph)

EXPERIMENTAL

All the starting materials and solvents were purified by standard procedures. ^{1}H NMR spectra were measured in deuteriochloroform solution on Tesla BS 587 instrument at 80 MHz, using tetramethylsilane as an internal standard (δ, ppm; *J*, Hz). UV-VIS spectra were measured by Hewlett–Packard diode array spectrophotometer 8452A in methanolic solution. Phenyl benzoates and phenyl phenylacetates were prepared by standard procedures[2].

General Procedure for Complexation of Phenyl Benzoates and Phenylacetates

The reaction mixture which consisted of the appropriate ester and $Cr(CO)_6$ in the molar ratio 3 : 1 in decalin was purged for 20 min with argon, then it was evacuated and again argon was passed through it. This procedure was repeated 2 – 3 times. After that, the reaction mixture was refluxed (bath temperature ≈ 260 °C) until the evolution of CO or decomposition of the complex started. All experiments were carried out with 0.5 g (2 mmol) of $Cr(CO)_6$. The reaction mixture was cooled to 20 °C, filtered through Kieselguhr, and then chromatographed under N_2 on SiO_2 column using 2-methylpentane as the eluent for elution of decalin and then a mixture of 2-methylpentane–ethyl acetate (5 : 1 to 4 : 1, v/v) for elution of the reaction products. The results are given in Tables I and II.

(η^6-Phenyl)tricarbonylchromium benzoate (IIIa). The complexation of phenol (0.27 g, 2.8 mmol) with $Cr(CO)_6$ (0.5 g, 2.2 mmol) was carried out as described above. After the complexation was over, the reaction mixture was cooled to 20 °C, and K_2CO_3 (0.5 g, 36 mmol) and benzoyl chloride (0.8 g, 5.7 mmol) were added under stirring. The mixture was stirred for 20 min at 45 °C, cooled to 20 °C and chromatographed. Chromatography afforded 0.16 g (24%) of (η^6-phenyl)tricarbonylchromium

benzoate. Crystallization from mixture of 2-methylpentane–ethyl acetate (9 : 1, v/v) yielded yellow crystals melting at 129 – 130.5 °C.

(η⁶-Phenyl)tricarbonylchromium phenylacetate (VII). The experiment was carried out as described for the synthesis of *IIIa*, except that 0.5 g of K_2CO_3 and 0.6 g (0.4 mmol) of phenylacetyl chloride were added to the (η⁶-phenol)tricarbonylchromium solution. Chromatography yielded 0.10 g (14.5%) of (η⁶-phenyl)tricarbonylchromium phenylacetate (*VII*) as yellow crystals from 2-methylpentane–ethyl acetate (9 : 1, v/v) melting at 96 – 97.5 °C.

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