ON THE SYNTHESIS OF 2-SUBSTITUTED (η^6-INDAN-1,3-DIONE)TRICARBONYLCHROMIUM COMPLEXES

Peter HRNCIAR, Pavel HRNCIAR, Vladimir GAJDA, Eva SVANYGOVA and Stefan TOMA[1]

Department of Organic Chemistry, Comenius University, 842 15 Bratislava, Slovak Republic; e-mail: [1] toma@fns.uniba.sk

Received June 28, 1996
Accepted November 8, 1996

Dedicated to the memory of the late Dr Zdenek Arnold.

Classical methods for the synthesis of indan-1,3-dione derivatives failed when applied to their tricarbonylchromium complexes. The desired 2-substituted (η^6-indan-1,3-dione)tricarbonylchromium complexes were prepared starting from protected indan-1,3-dione derivatives such as bis(dioxolanes) and enol ethers. Tricarbonylchromium complexes of indan-1,3-dione having at least one hydrogen at C-2 are unstable. Nevertheless, ethylation of 2-methyl(η^6-indan-1,3-dione)tricarbonylchromium and methylation of 2-ethyl(η^6-indan-1,3-dione)tricarbonylchromium were possible and proceeded with high stereoselectivity.

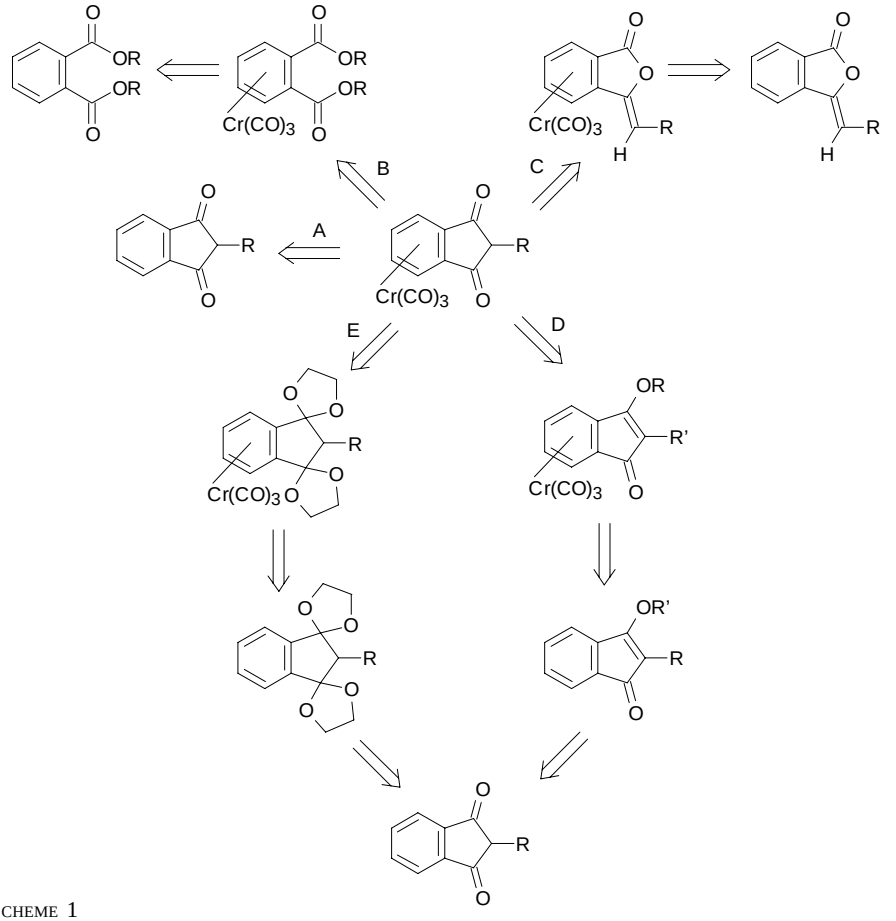
Key words: Indan-1,3-dione; Tricarbonylchromium complexes.

2-Substituted (η^6-indan-1,3-dione)tricarbonylchromium derivatives have been studied[1–3] for their anticoagulant properties. Some derivatives, such as 2-phenylindan-1,3-dione (Atrambone) or 2-(diphenylacetyl)indan-1,3-dione (Diphacinone), have been used in human medicine. Some indan-1,3-dione derivatives have also rodenticide properties[4]. Anions derived from 2-substituted indan-1,3-diones are interesting ambident nucleophiles, and their alkylation has been thoroughly studied[5–7].

The aim of the present study has been to find methods for the synthesis of tricarbonylchromium complexes of 2-substituted indan-1,3-diones and to investigate their anions as ambident nucleophiles.

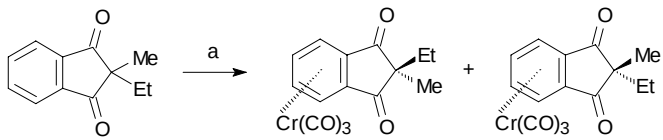
Five possible synthetic methods (A–E, Scheme 1) were chosen for the preparation of 2-substituted (η^6-indan-1,3-dione)tricarbonylchromium complexes. The routes B and C are most frequently used for the synthesis of 2-substituted indan-1,3-diones whereas methods D and E are not used in the classical synthesis of these compounds.

Direct complexation of indan-1,3-dione derivatives by our method[8], which consists in refluxing the starting material with hexacarbonylchromium in decalin, failed in most cases. The only exception was 2-ethyl-2-methylindan-1,3-dione (**1**) that gave a reason-



SCHEME 1

able yield (62%) of the desired product **2** as a 1.4 : 1 mixture of stereoisomers (Scheme 2). The isomers were separated by careful chromatography on silica gel using isohexane–ethyl acetate (4 : 1) mixture as eluent. In the main isomer the ethyl group is *trans* to the



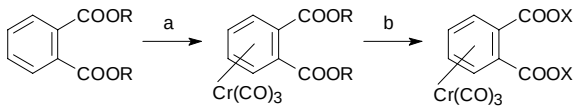
1 **2a** **2b**

a) $Cr(CO)_6$, decalin, Δ

SCHEME 2

$Cr(CO)_3$ group as concluded from the results of alkylation of monosubstituted derivatives (*vide infra*). In other cases, the reaction mixture turned green when refluxed for a short time in decalin, which was an unambiguous sign of complex decomposition.

2-Substituted indan-1,3-diones are frequently prepared by Claisen condensation of dimethyl or diethyl phthalate with alkyl esters of the appropriate alkanoic acids[9,10]. Our unsuccessful attempts to synthesize the tricarbonylchromium complexes are summarized in Scheme 3. Complexation of dimethyl or diethyl phthalate caused no problem, leading to compounds **4a** and **4b** in high yields. Subsequent reaction with ethyl acetate using *t*-BuOK as the catalyst failed. Only the η^6-tricarbonylchromium complex



3	R
a	Me
b	Et

4	R
a	Me
b	Et

	X
5	K
6	H

a) $Cr(CO)_6$, decalin, Δ; b) 1.CH_3COOEt, *t*-BuOK, THF, refl.; 2. aq. HCl

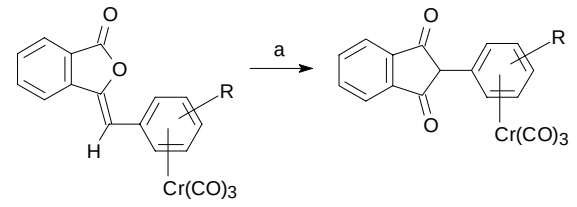
SCHEME 3

of potassium phthalate **5** was formed which was converted to the acid **6**. We assume an S_N2 reaction at the carbon atom of the alkoxy group, facilitated by the electron withdrawing effect of the tricarbonylchromium moiety. Under similar conditions, Claisen condensation of ethyl tricarbonylchromium(η^6-benzoate) produced ethyl (η^6-benzoyl)acetate tricarbonylchromium but we were not able to isolate the product in the pure state because of its decomposition. Similar experiments with methyl (η^6-benzoate)tricarbonylchromium produced only (η^6-benzoic acid)tricarbonylchromium. One could speculate whether these results are due to instability of the desired complexes caused by the presence of acidic hydrogen on C-2 of the indan-1,3-dione skeleton, or due to the internal strain in this condensed system. (The C–C bonds in benzenetricarbonylchromium complexes are 0.1 pm longer than in benzene.) The latter explanation is indirectly supported by similar behaviour of dimethyl thiophene-2, 3-dicarboxylate[11].

The phthalide–indandione rearrangement (route C) is the most frequently used approach to 2-arylindan-1,3-diones, but it was also used for the synthesis of 2-alkylindan-1,3-dione derivatives[12–14]. As we reported earlier[15], it is difficult to prepare a phthalide complex which has a $Cr(CO)_3$ group on the phthalide moiety. For this reason we also examined phthalides containing $Cr(CO)_3$ (Scheme 4).

The 3-benzylidenephthalide to indan-1,3-dione rearrangement proceeded without problems when the tricarbonylchromium group was bonded to the phenyl ring and 2-(η^6-substituted phenyltricarbonylchromium)indan-1,3-diones (**8a–8c**) were obtained

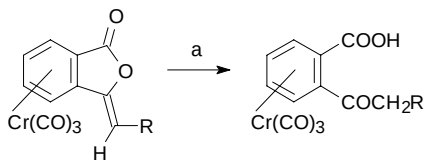
in high yields as deep-blue to black powders. Attempted purification by column chromatography on SiO_2 led to decomposition. Phthalide complexes **9a** and **9b** reacted with methoxide anion, but the intermediate keto ester was hydrolyzed to the free acids **10a** and **10b** under the work-up conditions.



7 **8**

a) MeONa, MeOH

7, 8	R
a	H
b	4-OMe
c	3-F



9 **10**

a) 1. MeONa, MeOH; 2. aq. HCl

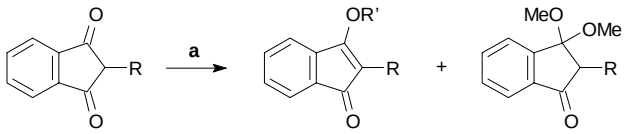
9, 10	R
a	CH_3
b	3,5-$F_2C_6H_3$

SCHEME 4

After these unsuccessful experiments we turned our attention to derivatives with protected groups: enol ethers and bis(dioxolanes) (routes D and E). Already at the very beginning of route D (Scheme 5) we encountered some problems. Under standard conditions used for cyclohexane-1,3-dione enol ether synthesis[16] (short reflux with a mixture of alcohol and hydrochloric acid) we obtained a complex mixture of products. 3-Methoxy-2-inden-1-ones could be prepared by the reaction of indan-1,3-dione derivatives with diazomethane[17]. By analogy with the published[18] procedure, we treated 2-substituted indan-1,3-diones with the appropriate alcohol at reflux in the presence of toluenesulfonic acid as catalyst, using the corresponding trialkyl orthoformate as the water scavenger. This method gave good yields of the desired enols **12a–12c**. The synthesis of 2-substituted 3-methoxy-2-inden-1-ones was not a selective reaction under these conditions either. In the preparation of 3-methoxy-2-methyl-2-inden-1-one we isolated 3,3′-dimethoxy-2-methyl-1-indanone (**13a**) as by-product and 3,3′-dimethoxy-

2-ethyl-1-indanone (**13b**) was even the main product of the reaction with 2-ethylindan-1,3-dione.

Complexation of the enol ethers with $Cr(CO)_6$ by our method[8] gave reasonable yields of complexes **14a–14d**. In the case of complexation of 3-ethoxy- as well as 3-methoxy-2-phenyl-2-inden-1-one, both the possible complexes (**14d**, **14e** and **15d**, **15e**) were isolated in comparable yields. Small amounts (up to 2%) of bis(tricarbonylchromium)

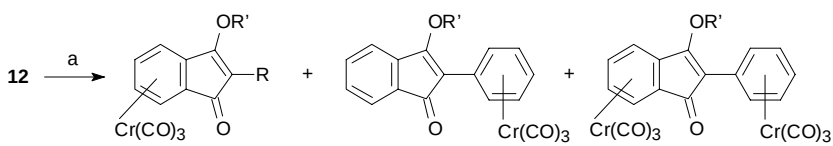


11	R
a	Me
b	Et
c	Ph

12	R	R'
a	Me	Me
b	Et	Me
c	Et	Et
d	Ph	Me
e	Ph	Et

13	R
a	Me
b	Et

a) R'OH, TsOH, $HC(OMe)_3$, refl.



14	R	R'
a	Me	Me
b	Et	Me
c	Et	Et
d	Ph	Me
e	Ph	Et

15	R'
d	Me
e	Et

16	R'
d	Me
e	Et

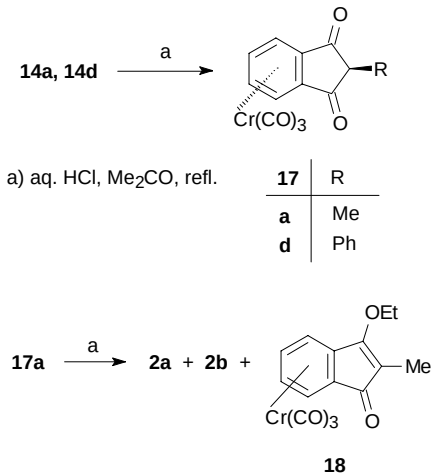
a) $Cr(CO)_6$, decalin, Δ

SCHEME 5

complexes **16d** and **16e** were also isolated. Attempted preparation of the complex from 3,3-dimethoxy-1-indanone failed. A mixture of approximately nine products was detected by TLC and about 50% of the starting material was destroyed by polymerization.

Compound **14a** was smoothly hydrolyzed with a mixture of 6 M HCl and acetone, in analogy to the described procedure[19], and the desired **17a** was obtained in 75% yield upon flash chromatography. Alkylation with ethyl iodide gave a mixture of 2-ethyl-2-

methyl(η^6-indan-1,3-dione)tricarbonylchromium (**2b**) as the single stereoisomer (according to ^{1}H NMR spectrum), together with the *O*-alkylation product **18**. The ratio of the *C*- to *O*-alkylation products was 5 : 1. Compound **15d** was hydrolyzed to give the same product (**8a**) as was isolated from the phthalide–indandione rearrangement (Scheme 6).



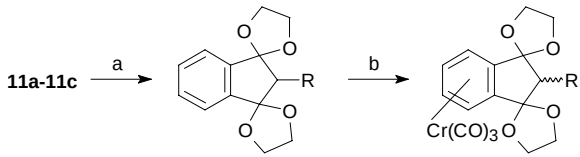
SCHEME 6

A synthesis of bis(dioxolane) from indan-1,3-dione has been described[20], but with a rather low yield. We therefore used a method analogous to that used for the synthesis of enol ethers and reasonable yields (20–50%) of the desired bis(dioxolanes) **19a–19c** were thus obtained (Scheme 7). Interestingly, in the preparation of bis(dioxolane) from 2-ethylindan-1,3-dione the main product was the mono(dioxolane).

Complexation of dioxolanes **19a–19c** caused no problems. Compounds **19a** and **19b** gave mixtures of both possible stereoisomers in the ratio 2.1 : 1 and 8 : 1, respectively. We assume, that in the main isomer the R group is *trans* to $Cr(CO)_3$. Complexation of **19c** (R = phenyl) resulted in two products, **20c** and **21**, in the ratio 8 : 1, the main isomer having the $Cr(CO)_3$ moiety on the 2-phenyl group.

The dioxolane complexes **20a** and **20b** were hydrolyzed with 6 M HCl–acetone mixture at 50 °C. The course of the hydrolysis was monitored by TLC and the colour of the reaction mixture changed from yellow to red. Since in the usual work-up of the reaction mixture decomplexation started immediately after contact with aqueous potassium carbonate, we omitted washing with potassium carbonate solution and dilute acid. This, together with rapid work-up, gave the desired products **17a** and **17b** in reasonable to good yields. The reaction afforded only a single isomer, most probably with the R group *trans* to $Cr(CO)_3$.

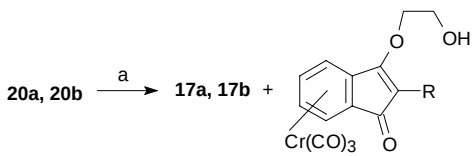
Another set of complexes which we isolated were 2-alkyl-3-hydroxyethoxy(η^6-2-inden-1-one)tricarbonylchromiums **22a** and **22b**. Their formation pointed also to the fact that there is some internal strain in the desired complexes **17a** and **17b**.



19 **20**

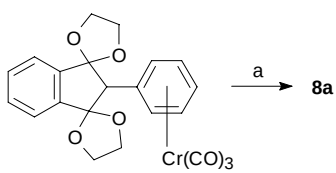
19, 20	R
a	Me
b	Et
c	Ph

a) $(CH_2OH)_2$, TsOH, $CH(OMe)_3$, $CHCl_3$, refl.; b) $Cr(CO)_6$, decalin, Δ



22	R
a	Me
b	Et

a) aq. HCl, acetone, 50 °C



21

a) aq. HCl, acetone, 50 °C

SCHEME 7

Alkylation of 2-methyl(η^6-indan-1,3-dione)tricarbonylchromium with ethyl iodide resulted in formation of both the *C*- and *O*-alkylation product **2a** and **18** in the ratio 5 : 1. In the alkylation of 2-ethyl(η^6-indan-1,3-dione)tricarbonylchromium with methyl iodide only the *C*-alkylation product was formed. These results suggest that the alkyla-

tion is stereoselective, similarly to the addition of Grignard reagent to (η^6-indan-2-one)tricarbonylchromium[19].

EXPERIMENTAL

Melting points were measured on a Kofler hot stage and are uncorrected. ^{1}H NMR spectra (δ, ppm; *J*, Hz) were recorded on a 80 MHz Tesla 487 A instrument with $CDCl_3$ as solvent and tetramethylsilane as internal standard.

3-[η^6-(*p*-Methoxybenzylidene)]tricarbonylchromium phthalide (**7b**), (η^6-3-ethylindenephthalide)tricarbonylchromium (**9a**), [3-(3,5-difluorobenzylidene)(η^6-phthalide)]tricarbonylchromium (**9b**) as well as 3-(η^6-benzylidene)tricarbonylchromium phthalide (**7a**) were prepared according to ref.[15]. 2-Methyl-, 2-ethyl- and 2-phenylindandione (**11a–11c**) were prepared as described[12,14]. All experiments were carried out under dry argon atmosphere.

Complexation of the ligands was performed using the described[8] method and afforded complexes **2a**, **2b**, **4a**, **4b**, **13a**, **14a–14e**, **15d**, **15e**, **16a**, **16d**, **20a–20c**, and **21**.

2-Ethyl-2-methylindan-1,3-dione (**1**)

Sodium metal in small pieces (2.3 g, 0.1 mol) was dissolved in absolute ethanol (100 ml). 2-Methylindan-1,3-dione (11.3 g, 0.07 mol) was added and the rection mixture was refluxed. Ethyl iodide (15.6 g, 0.09 mol) was slowly added and the mixture was refluxed for another 6 h. The solution was filtered and concentrated to a half and water (10 ml) was added. The product, 2-ethyl-2-methylindan-1,3-dione (**1**), was isolated as white crystals (6.58 g, 50%), m.p. 45–47 °C. For $C_{12}H_{12}O_2$ (188.2) calculated: 76.57% C, 6.42% H; found: 76.72% C, 6.39% H. ^{1}H NMR spectrum: 0.74 t, 3 H (CH_3); 1.27 s, 3 H (CH_3); 1.87 q, 2 H (CH_2); 7.85–8.0 m, 4 H (C_6H_4).

Attempted Preparation of (η^6-Indan-1,3-dione)tricarbonylchromium from 1,2-Bis(methoxycarbonyl-η^6-benzene)tricarbonylchromium (**4**)

Complex **4** (0.5 g, 2.5 mmol) and ethyl acetate (0.22 g, 2.5 mmol) were dissolved in dry THF (20 ml). Potassium *tert*-butoxide (0.4 g, 3.6 mmol) was added and the reaction mixture was refluxed for 5 h. Potassium (η^6-benzene)tricarbonylchromium-1,2-dicarboxylate (**5**) (0.9 g, 95%), which deposited as a yellow solid, was collected on filter and washed with diethyl ether. It was dissolved in water (20 ml) and the solution was acidified with hydrochloric acid. The precipitated (η^6-benzene)tricarbonylchromium-1,2-dicarboxylic acid (**6**) was filtered and dried at 40 °C/133.3 Pa. Yellow solid, m.p. 160 °C (0.65 g, 80%). For $C_{11}H_6CrO_7$ (302.2) calculated: 43.73% C, 2.00% H; found: 43.87% C, 1.95% H. ^{1}H NMR spectrum: 5.73–6.05 m, 4 H ($C_6H_4Cr(CO)_3$); 8.69 s, 2 H (COOH).

2-(η^6-Phenyltricarbonylchromium)indan-1,3-dione (**8a**)

3-(η^6-Benzylidenetricarbonylchromium)phthalide (0.5 g, 1.4 mmol) was added to a solution of sodium methoxide prepared from Na (0.1 g) and dry methanol (20 ml). After reflux for 2 h, the reaction mixture was cooled to room temperature and neutralized with 5 M HCl. The product was extracted into diethyl ether, the ethereal solution was washed with water, dried over anhydrous Na_2SO_4, filtered and concentrated till 2-(η^6-phenyltricarbonylchromium)indan-1,3-dione started to separate. Deep-red crystals (0.45 g, 90%), m.p. 180 °C. For $C_{18}H_{10}CrO_5$ (358.3) calculated: 60.34% C, 2.80% H; found: 60.14% C, 2.95% H. ^{1}H NMR spectrum: 4.01 s, 1 H (CHPh); 5.32 m, 3 H ($ArCr(CO)_3$); 5.62 m, 2 H ($ArCr(CO)_3$); 8.00 m, 4 H (C_6H_4 – a doublet at 7.98, J = 6 can be distinguished).

2-(η^6-4-Methoxyphenyltricarbonylchromium)indan-1,3-dione (**8b**)

The title compound was prepared in a 54% yield from 3-(η^6-4-methoxybenzylidenetricarbonylchromium)phthalide by the same procedure as described above. Black crystals, m.p. >300 °C. For $C_{19}H_{12}CrO_5$ (388.3) calculated: 58.77% C, 3.11% H; found: 58.34% C, 3.58% H. ^{1}H NMR spectrum: 3.70 s, 3 H (OCH_3); 3.92 s, 1 H (CHAr); 5.05 d, 2 H, J = 7 ($ArCr(CO)_3$); 5.84 d, 2 H, J = 7 ($ArCr(CO)_3$); 7.97 m, 4 H (C_6H_4 – a doublet at 7.97, J = 6 can be distinguished).

2-(η^6-3-Fluorophenyltricarbonylchromium)indan-1,3-dione (**8c**)

The title compound was prepared in a 62% yield from 3-(η^6-3-flurobenzylidenetricarbonylchromium)phthalide by the same procedure as described above. Deep-red crystals, m.p. >360 °C. For $C_{18}H_9CrFO_5$ (367.2) calculated: 58.87% C, 2.47% H; found: 59.11% C, 2.64% H. ^{1}H NMR spectrum: 3.80 bs, 1 H ($ArCr(CO)_3$); 4.27 bs, 3 H ($ArCr(CO)_3$); 8.80 m, 4 H (C_6H_4, doublet at 7.99, J = 6 can be distinguished).

η^6-(2-Propionylbenzene)tricarbonylchromiumcarboxylic Acid (**10a**)

The rearrangement of η^6-(2-ethylidenephthalide)tricarbonylchromium was performed by the same procedure as described above. After acidification of the reaction mixture, the methanol was evaporated and the product extracted into chloroform. Evaporation of the chloroform gave red crystals (23%) of η^6-(2-propionylbenzene)tricarbonylchromiumcarboxylic acid (**10a**), m.p. 170 °C. For $C_{13}H_{10}CrO_6$ (314.2) calculated: 49.69% C, 3.22% H; found: 49.34% C, 3.19% H. ^{1}H NMR spectrum: 1.20 bt, 3 H (CH_3); 2.12 bs, 1 H (COOH); 2.80 bq, 2 H (CH_2); 5.37 m, 2 H ($ArCr(CO)_3$); 5.90 m, 2 H ($ArCr(CO)_3$).

2-(3,5-Difluorophenylacetyl)(η^6-benzene)tricarbonylchromiumcarboxylic Acid (**10b**)

The title compound was prepared in 63% yield from 3-(3,5-difluorobenzylidene)(η^6-phthalide)tricarbonylchromium (**9b**) by the same procedure as described above. Black solid, m.p. >360 °C. For $C_{18}H_8F_2CrO_5$ (394.3) calculated: 54.84% C, 2.05 % H; found: 55.32% C, 2.15% H. ^{1}H NMR spectrum: 3.70 bs, 1 H (COOH); 4.22 s, 2 H ($COCH_2$); 5.70 m, 2 H ($ArCr(CO)_3$); 5.97 m, 2 H ($ArCr(CO)_3$); 6.37 m, 1 H ($C_6H_3F_2$); 6.82 m, 2 H ($C_6H_3F_2$).

3-Methoxy-2-methyl-2-inden-1-one (**12a**)

2-Methylindan-1,3-dione (**11a**) (1.5 g, 0.01 mol) and trimethyl orthoformate (3.2 g, 0.03 mol) were dissolved in methanol (20 ml). *p*-Toluenesulfonic acid (100 mg) was added and the reaction mixture was refluxed for 3 h. The mixture was then poured into crushed ice, the organic material was extracted into diethyl ether, and the ethereal solution was washed with cold $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the oily residue (1.8 g, 95%) was crystallized from diethyl ether–isohexane (nearly pure isohexane). The yellow crystalline **12a**, m.p. 79–81 °C, was isolated in 75% yield. For $C_{11}H_{11}O_2$ (174.2) calculated: 75.84% C, 5.80% H; found: 76.05% C, 5.89% H. ^{1}H NMR spectrum: 2.01 s, 3 H (CH_3); 4.24 s, 3 H (OCH_3); 7.05–7.44 m, 4 H (C_6H_4). As the second product we isolated 3,3-dimethoxy-2-methylindan-1-one (**13a**), m.p. 69–74 °C (20%). For $C_{12}H_{14}O_3$ (206.25) calculated: 69.88% C, 6.84% H; found: 69.82% C, 7.03% H. ^{1}H NMR spectrum: 1.35 d, 3 H, J = 8 (CH_3); 2.93 q, 1 H (CH); 3.33 s, 3 H (OCH_3); 3.42 s, 3 H (OCH_3); 7.50–7.84 m, 4 H (C_6H_4).

2-Ethyl-3-methoxy-2-inden-1-one (**12b**)

The reaction was carried out as described above, starting from 2-ethylindan-1,3-dione (**11b**) (2 g, 0.01 mol) and trimethyl orthoformate (3.2 g, 0.03 mol). The yellow oily product (1.6 g; 70%) was purified by column chromatography to give oily 2-ethyl-3-methoxy-2-inden-1-one (**12b**) (20%). For $C_{12}H_{13}O_2$ (188.2) calculated: 76.61% C, 6.38% H; found: 76.45% C, 6.22% H. ^{1}H NMR spectrum: 1.11 t, 3 H (CH_3); 2.45 q, 2 H (CH_2); 4.22 s, 3 H (OCH_3); 7.07–7.25 m, 4 H (C_6H_4). As the second product we isolated 2-ethyl-3,3-dimethoxyindan-1-one (**13b**) (oil, 50%). For $C_{13}H_{16}O_3$ (220.3) calculated: 70.09% C, 7.38% H; found: 70.82% C, 6.94% H. ^{1}H NMR spectrum: 1.11 t, 3 H (CH_3); 1.75 m, 2 H (CH_2); 2.93 t, 2 H (CH); 3.32 s, 3 H (OCH_3); 3.65 s, 3 H (OCH_3); 7.26–7.70 m, 4 H (C_6H_4).

3-Ethoxy-3-ethyl-2-inden-1-one (**12c**)

2-Ethylindan-1,3-dione (**11b**; 4.5 g, 26 mmol) was dissolved in absolute ethanol (50 ml). The solution was saturated with gaseous HCl and left to stand at room temperature for 60 h. Hydrogen chloride was then neutralized with NaOH (5 pellets) and ethanol was evaporated under reduced pressure. The residue was dissolved in diethyl ether and the solution was washed with 30% NaOH. The ethereal solution was dried over anhydrous Na_2SO_4, filtered and the solvent evaporated. The remaining yellow oil was flash-chromatographed on an SiO_2 column in isohexane–ether (1 : 2). The obtained yellow oil was crystallized from ether–isohexane to give the product (2 g; 46%), m.p. 46–49 °C. For $C_{13}H_{14}O_2$ (202.2) calculated: 77.20% C, 6.93% H; found: 77.32% C, 6.72% H. ^{1}H NMR spectrum: 1.15 t, 3 H (CH_3); 1.48 t, 3 H (CH_3); 2.40 q, 2 H (CH_2); 4.52 q, 2 H (OCH_2); 7.25 m, 4 H (C_6H_4).

3-Methoxy-2-phenyl-2-inden-1-one (**12d**)

The reaction of 2-phenylindan-1,3-dione (**11c**; 1.3 g, 6 mmol) and trimethyl orthoformate (3.2 g, 30 mmol) gave 1.5 g (90%) of yellow crystalline product, m.p. 78–81 °C (ether–isohexane). For $C_{16}H_{12}O_2$ (236.2) calculated: 81.36% C, 5.08% H; found: 81.48% C, 5.20% H. ^{1}H NMR spectrum: 3.87 s, 3 H (OCH_3); 7.20–7.54 m, 9 H (C_6H_4 + C_6H_5).

3-Ethoxy-2-phenyl-2-inden-1-one (**12e**)

The reaction was carried out as described above. Starting from 2-phenylindan-1,3-dione (**11c**; 1.10 g, 5 mmol) and triethyl orthoformate (3.5 g, 30 mmol), yellow crystalline material (0.7 g; 56.5%) was isolated; m.p. 69–70 °C. For $C_{17}H_{14}O_2$ (250.2) calculated: 81.61% C, 5.64% H; found: 81.49% C, 5.71% H. ^{1}H NMR spectrum: 1.28 t, 3 H (CH_3); 4.13 q, 2 H (CH_2); 7.52 m, 9 H (C_6H_4 + C_6H_5).

1,3-Bis(ethylenedioxy)-2-methylindan (**19a**)

A solution of 2-methylindan-1,3-dione (**11a**; 1.5 g, 10 mmol), ethylene glycol (4.8 ml), trimethyl orthoformate (3.2 g, 30 mmol) and *p*-toluenesulfonic acid (300 mg) in chloroform (20 ml) was refluxed for 24 h. After cooling to room temperature, chloroform (100 ml) was added, the solution was extracted with 20% NaOH (5 × 50 ml), dried over Na_2SO_4, filtered and the solvent was evaporated. Crystallization from diethylether–isohexane gave white crystals (1.5 g; 50%), m.p. 97–98.5 °C. For $C_{14}H_{16}O_4$ (248.2) calculated: 67.73% C, 6.49% H; found: 67.92% C, 6.32% H. ^{1}H NMR spectrum: 1.10 d, 3 H, J = 7 (CH_3); 2.72 q, 1 H (CH); 4.17 m, 8 H (OCH_2); 7.35 s, 4 H (C_6H_4).

1,3-Bis(ethylenedioxy)-2-ethylindan (**19b**)

The compound was prepared from 2-ethylindan-1,3-dione (**11b**; 1.5 g, 8 mmol), ethylene glycol (2 ml), TsOH (250 mg) and trimethyl orthoformate (3.2 g, 30 mmol) as described for **19a**. Yield 0.4 g (20%) of white crystals, m.p. 90–92 °C (diethyl ether). For $C_{15}H_{18}O_4$ (262.3) calculated: 68.68% C, 6.92% H; found: 68.43% C, 6.87% H. ^{1}H NMR spectrum: 1.05 t, 3 H (CH_3); 1.68 q, 2 H (CH_2); 2.61 t, 1 H (CH); 4.16 m, 8 H (OCH_2); 7.33 bs, 4 H (C_6H_4).

1,3-Bis(ethylenedioxy)-2-phenylindan (**19c**)

The experiment was carried out as described above. Reaction of 2-phenylindan-1,3-dione (**11c**; 2.1 g, 0.01 mol), ethylene glycol (4.8 ml) and trimethyl orthoformate (2.4 g, 20 mmol) afforded 2.1 g (72%) of 1,3-bis(ethylenedioxy)-2-phenylindan (**19c**) as white crystals, m.p. 152–154 °C. For $C_{19}H_{18}O_4$ (310.3) calculated: 73.63% C, 5.82% H; found: 73.81% C, 5.62% H. ^{1}H NMR spectrum: 3.52 s, 1 H (CH); 3.67 m, 4 H (OCH_2); 4.05 m, 4 H (OCH_2); 7.32 m, 5 H (C_6H_5).

Complexation of Compounds **1**, **3**, **12**, and **19**

Direct complexation was carried out by heating indandione **1**, alkyl phthalates **3**, indenones **12** and dioxolanes **19** with hexacarbonylchromium in decalin for 0.5–3.5 h according to ref.[8].

2-Ethyl-2-methyl(η^6-indan-1,3-dione)tricarbonylchromium (**2a**, **2b**)

Complexation of indandione **1** afforded a mixture of **2a** and **2b** as yellow-orange crystals in 62% yield. For $C_{15}H_{12}CrO_5$ (324.2) calculated: 55.56% C, 3.72% H; found: 56.19% C, 3.74% H. Careful chromatography afforded:

2a (*threo*), m.p. 78–79 °C. ^{1}H NMR spectrum: 0.83 t, 3 H (CH_3); 1.39 s, 3 H (CH_3); 1.87 q, 2 H (CH_2); 5.62 d, J = 8 and 5.62 d, J = 3, 2 H ($ArCr(CO)_3$); 5.92 d, J = 8 and 5.92 d, J = 3, 2 H ($ArCr(CO)_3$).

2b (*erythro*), m.p. 121–123 °C. ^{1}H NMR spectrum: 0.96 t, 3 H (CH_3); 1.30 s, 3 H (CH_3); 1.87 q, 2 H (CH_2); 5.62 d, J = 8 and 5.62 d, J = 3, 2 H ($ArCr(CO)_3$); 5.92 d, J = 8 and 5.92 d, J = 3, 2 H ($ArCr(CO)_3$).

Dimethyl (η^6-Benzene)tricarbonylchromium-1,2-dicarboxylate (**4a**)

Complexation of **3a** afforded **4a** in 73% yield as deep-red crystals, m.p. 58.5–59.5 °C. For $C_{13}H_{10}CrO_7$ (330.2) calculated: 47.28% C, 3.05% H; found: 47.10% C, 3.01% H. ^{1}H NMR spectrum: 3.90 s, 6 H (OCH_3); 5.35 m, 2 H ($ArCr(CO)_3$); 5.65 m, 2 H ($ArCr(CO)_3$. Besancon[21] obtained this compound in 55% yield.

Diethyl (η^6-Benzene)tricarbonylchromium-1,2-dicarboxylate (**4b**)

Complexation of **3b** afforded **4b** (82%) as deep-red crystals, m.p. 51–52 °C. For $C_{15}H_{14}CrO_7$ (358.3) calculated: 52.28% C, 3.94% H; found: 54.49% C, 3.97% H. ^{1}H NMR spectrum: 1.36 t, 6 H (CH_3); 4.34 q, 4 H (OCH_2); 5.40 bs, 2 H ($ArCr(CO)_3$); 5.67 bs, 2 H ($ArCr(CO)_3$).

3-Methoxy-2-methyl[η^6-(2-inden-1-one)]tricarbonylchromium (**14a**)

Complexation of **12a** afforded **14a** (25%) as violet crystals, m.p. 142–146 °C. For $C_{14}H_{10}CrO_5$ (310.2) calculated: 54.20% C, 3.24% H; found: 54.37% C, 3.26% H. ^{1}H NMR spectrum: 2.03 s, 3 H

(CH_3); 4.21 s, 3 H (OCH_3); 5.30 m, 1 H ($ArCr(CO)_3$); 5.54 d, 2 H, J = 4 ($ArCr(CO)_3$); 6.02 d, 1 H, J = 6 ($ArCr(CO)_3$).

2-Ethyl-3-methoxy[η^6-(2-inden-1-one)]tricarbonylchromium (**14b**)

Complexation of **12b** afforded **14b** (22%) as violet crystals, m.p. 132–135 °C. For $C_{15}H_{12}CrO_5$ (324.0) calculated: 55.56% C, 3.72% H; found: 55.94% C, 3.80% H. ^{1}H NMR spectrum: 1.12 t, 3 H (CH_3); 2.46 q, 2 H (OCH_2); 4.18 s, 3 H (OCH_3); 5.25 m, 1 H ($ArCr(CO)_3$); 5.50 m, 2 H ($ArCr(CO)_3$); 6.00 d, 1 H, J = 6 ($ArCr(CO)_3$).

2-Ethyl-3-ethoxy(η^6-2-inden-1-one)tricarbonylchromium (**14c**)

Complexation of **12c** afforded **14c** (18%) as violet crystals, m.p. 125–127 °C. For $C_{16}H_{14}CrO_5$ (338.1) calculated: 56.80% C, 4.14% H; found: 56.53% C, 4.13% H. ^{1}H NMR spectrum: 1.10 t, 3 H (CH_3); 1.46 t, 3 H (CH_3); 2.41 q, 2 H (CH_2); 4.46 q, 2 H (OCH_2); 5.30 m, 1 H ($ArCr(CO)_3$); 5.52 m, 2 H ($ArCr(CO)_3$); 5.61 d, 1 H, J = 6 ($ArCr(CO)_3$).

Complexation of compound **12d** afforded a mixture of **14d** (39%), **15d** (39%), and **16d** (2%).

3-Methoxy-2-phenyl[η^6-(2-inden-1-one)]tricarbonylchromium (**14d**), brown crystals, m.p. 165 °C (dec.). For $C_{19}H_{12}CrO_5$ (372.3) calculated: 61.29% C, 2.97% H; found: 60.73% C, 3.20% H. ^{1}H NMR spectrum: 3.79 s, 3 H (OCH_3); 5.41 t, 1 H ($ArCr(CO)_3$); 5.62 t, 1 H ($ArCr(CO)_3$); 5.61 d, 1 H, J = 6 ($ArCr(CO)_3$); 6.10 d, 1 H, J = 6 ($ArCr(CO)_3$); 7.35 bs, 5 H (C_6H_5).

3-Methoxy-2-(η^6-phenyltricarbonylchromium)-2-inden-1-one (**15d**), violet crystals, m.p. 153.4–154.5 °C. For $C_{19}H_{12}CrO_5$ (372.3) calculated: 61.29% C, 2.97% H; found: 61.08% C, 3.28% H. ^{1}H NMR spectrum: 4.45 s, 3 H (OCH_3); 5.36 m, 3 H ($ArCr(CO)_3$); 6.12 m, 2 H ($ArCr(CO)_3$); 7.46 m, 4 H (C_6H_4).

3-Methoxy-2-(η^6-phenyltricarbonylchromium)[η^6-(2-inden-1-one)]tricarbonylchromium (**16d**), black-violet crystals, m.p. 137–142 °C (dec.). For $C_{22}H_{12}Cr_2O_8$ (508.3) calculated: 51.98% C, 2.38% H; found: 51.54% C, 2.41% H. ^{1}H NMR spectrum: 4.25 s, 3 H ($COCH_3$); 5.37 m, 3 H ($ArCr(CO)_3$); 5.55 m, 2 H ($ArCr(CO)_3$); 5.95 m, 4 H ($ArCr(CO)_3$).

Complexation of compound **12e** afforded a mixture of **14e** (21%), **15e** (12%), and **16e** (2%).

3-Ethoxy-2-phenyl[η^6-(2-inden-1-one)]tricarbonylchromium (**14e**), brown crystals, m.p. 115–117 °C. For $C_{20}H_{14}CrO_5$ (384.4) calculated: 62.17% C, 3.65% H; found: 62.90% C, 3.52% H. ^{1}H NMR spectrum: 1.25 t, 3 H (CH_3); 4.04 q, 2 H (OCH_3); 5.30 dt, 1 H ($ArCr(CO)_3$); 5.57 m, 2 H ($ArCr(CO)_3$); 6.10 d, 1 H, J = 5 ($ArCr(CO)_3$); 7.35 bs, 5 H (C_6H_5).

3-Ethoxy-2-(η^6-phenyltricarbonylchromium)-2-inden-1-one (**15e**), violet crystals, m.p. 152–154 °C. For $C_{20}H_{14}CrO_5$ (384.4) calculated: 62.17% C, 3.65% H; found: 61.88% C, 3.44% H. ^{1}H NMR spectrum: 1.62 t, 3 H (CH_3); 4.79 q, 2 H (OCH_3); 5.37 m, 3 H ($ArCr(CO)_3$); 6.14 dd, 2 H, J = 7 ($ArCr(CO)_3$); 7.40 bs, 4 H (C_6H_4).

3-Ethoxy-2-(η^6-phenyltricarbonylchromium)[η^6-(2-inden-1-one)]tricarbonylchromium (**16e**), black-violet crystals, m.p. 137–140 °C. For $C_{23}H_{14}Cr_2O_8$ (520.4) calculated: 53.08% C, 2.51% H; found: 53.39% C, 2.78% H. ^{1}H NMR spectrum: 1.59 t, 3 H (CH_3); 4.50 q, 2 H (OCH_2); 5.25–6.21 m, 9 H ($ArCr(CO)_3$).

1,3-Bis(ethylenedioxy)-2-methyl(η^6-indan)tricarbonylchromium (**20a**)

Complexation of **19a** afforded **20a** (71%) as yellow crystals, m.p. >169 °C (dec.). For $C_{17}H_{15}CrO_5$ (384.3) calculated: 53.15% C, 4.19% H; found: 52.75% C, 4.15% H. ^{1}H NMR spectrum: 1.07 m (two overlapped t), 3 H (CH_3); 2.38 q, 0.33 H (CHR); 2.90 q, 0.66 H (CHR); 4.16 bs, 8 H (OCH_2); 5.30 bs, 2 H ($ArCr(CO)_3$); 5.43 bs, 2 H ($ArCr(CO)_3$).

1,3-Bis(ethylenedioxy)-2-ethyl(η^6-indan)tricarbonylchromium (**20b**)

Complexation of **19b** afforded **20b** (82%) as yellow crystals, m.p. 184–186 °C. For $C_{18}H_{17}CrO_5$ (398.3) calculated: 54.27% C, 4.55% H; found: 54.64% C, 4.61% H. ^{1}H NMR spectrum: 1.02 t, 3 H (CH_3); 1.62 m, 2 H (CH_2); 2.13 t, 0.05 H (CHR); 2.75 t, 0.95 H (CHR); 4.18 bs, 8 H (OCH_2); 5.27 bs, 2 H ($ArCr(CO)_3$); 5.34 bs, 2 H ($ArCr(CO)_3$). Crystallization from isohexane gave single major isomer (2.75 t, 1 H (CHR)).

Complexation of **19c** afforded a mixture of **20c** (24%) and **21** (6%).

1,3-Bis(ethylenedioxy)-2-phenyl(η^6-indan)tricarbonylchromium (**20c**), yellow crystals, m.p. >150 °C (dec.). For $C_{22}H_{18}CrO_7$ (446.4) calculated: 59.19% C, 4.06% H; found: 59.01% C, 4.12% H. ^{1}H NMR spectrum: 3.50 m, 4 H (OCH_2); 3.80 s, 1 H (CH); 4.07 m, 4 H (OCH_2); 5.25 m, 2 H ($ArCr(CO)_3$); 5.42 m, 2 H ($ArCr(CO)_3$); 7.35 m, 3 H (C_6H_5); 7.57 m, 2 H (C_6H_5).

1,3-Bis(ethylenedioxy)-2-(η^6-phenyltricarbonylchromium)indan (**21**), yellow crystals, m.p. 188 °C (dec.). For $C_{22}H_{18}CrO_7$ (446.4) calculated: 59.19% C, 4.06% H; found: 58.92% C, 4.23% H. ^{1}H NMR spectrum: 4.15–4.30 m, 9 (OCH_2 + CHPh; app. triplet at 4.28); 5.17 t, 2 H ($ArCr(CO)_3$); 5.43 d, 1 H, J = 6 ($ArCr(CO)_3$); 5.73 d, 2 H, J = 6 ($ArCr(CO)_3$); 7.39 s, 4 H (C_6H_4).

Hydrolysis of Enol Ethers and Bis(dioxolanes) Derived from 2-Substituted (η^6-Indan-1,3-dione)tricarbonylchromium. General Procedure

The appropriate starting compound (1 mmol) was dissolved in a 2 : 1 mixture of acetone–6 M HCl (5 ml) and the reaction mixture was stirred at 40–50 °C. The course of the reaction was followed by TLC. After the reaction was over (10 min–2 h), the mixture was poured into ice-water and the product was extracted into diethyl ether. The ethereal solution was washed with water. The pH of the aqueous washings should be about 4.5, as the product was soluble in water at pH ≈ 7 and would decompose. The ethereal solution was dried over magnesium sulfate, the solvent was evaporated and the residue was flash-chromatographed on an SiO_2 column in isohexane–ethyl acetate.

2-Methyl(η^6-indan-1,3-dione)tricarbonylchromium (**17a**).

Method A. Prepared by hydrolysis of (2-methyl-3-methoxy-η^6-2-inden-1-one)tricarbonylchromium (**14a**) (time of hydrolysis 10 min) in 75% yield as red crystals, m.p. 145 °C (dec.). For $C_{13}H_8CrO_5$ (296.2) calculated: 52.71% C, 2.72% H; found: 52.46% C, 2.70% H. ^{1}H NMR spectrum: 1.45 d, 3 H (CH_3); 2.95 q, 1 H (CH); 5.66 bs, 2 H ($C_6H_4Cr(CO)_3$); 5.91 bs, 2 H ($C_6H_4Cr(CO)_3$).

Method B. Prepared by hydrolysis of 1,3-bis(ethylenedioxy)-2-methyl(η^6-indan)tricarbonylchromium (**20a**) (time of hydrolysis 2.5 h) in 77% yield and was identical with the material from the previous experiment. The second chromatographic band gave 2-methyl-3-(2-hydroxyethoxy)(η^6-2-inden-1-one)tricarbonylchromium (**22a**) (4%) as a red oil. For $C_{15}H_{12}CrO_6$ (340.2) calculated: 53.11% C, 3.27% H; found: 53.28% C, 3.31% H. ^{1}H NMR spectrum: 1.99 s, 3 H (CH_3); 4.00 t, 2 H (OCH_2); 4.55 t, 2 H (OCH_2); 5.30 m, 1 H ($C_6H_4Cr(CO)_3$); 5.33 d, 2 H, J = 3 ($C_6H_4Cr(CO)_3$); 6.03 d, 1 H, J = 6 ($C_6H_4Cr(CO)_3$).

2-Ethyl(η^6-indan-1,3-dione)tricarbonylchromium (**17b**). Prepared by hydrolysis of 1,3-bis(ethylenedioxy)-2-ethyl(η^6-indan)tricarbonylchromium (**20b**) (time of hydrolysis 2 h) in 15% yield as a red semisolid material. For $C_{14}H_{10}CrO_5$ (310.3) calculated: 54.19% C, 3.25% H; found: 54.62% C, 3.32% H. ^{1}H NMR spectrum: 1.12 t, 3 H (CH_3); 2.00 q, 2 H (CH_2); 2.95 t, 1 H (CH); 5.62 m, 2 H ($C_6H_4Cr(CO)_3$); 5.90 m, 2 H ($C_6H_4Cr(CO)_3$).

2-Ethyl-3-(2-hydroxyethoxy)(η^6-2-inden-1-one)tricarbonylchromium (**22b**) was isolated from the second band in 3.5% yield; red crystals, m.p. 103.5–105 °C. For $C_{16}H_{14}CrO_6$ (354.2) calculated: 54.40% C, 3.70% H; found: 54.23% C, 4.13% H. ^{1}H NMR spectrum: 1.17 t, 3 H (CH_3); 1.62 bs, 1 H (OH); 2.47 q, 2 H (CH_2); 4.06 t, 2 H (OCH_2); 4.52 t, 2 H (OCH_2); 5.32 m, 1 H ($C_6H_4Cr(CO)_3$); 5.62 app d, 2 H ($C_6H_4Cr(CO)_3$); 6.03 d, 1 H, J = 6 ($C_6H_4Cr(CO)_3$).

2-Phenyl(η⁶-indan-1,3-dione)tricarbonylchromium (**17d**). Prepared in 84% yield by hydrolysis of 3-methoxy-2-phenyl(η⁶-2-inden-1-one)tricarbonylchromium (**14d**) (time of hydrolysis 1.45 h); deep-blue crystals, m.p. 155 °C (dec.). For $C_{18}H_{12}CrO_5$ (358.2) calculated: 60.34% C, 2.81% H; found: 60.45% C, 2.93% H. ^{1}H NMR spectrum: 3.79 s, 1 H (CH); 5.37 bt, 1 H ($C_6H_4Cr(CO)_3$); 5.70 m, 2 H ($C_6H_4Cr(CO)_3$); 6.12 bt, 1 H ($C_6H_4Cr(CO)_3$); 7.35 bs, 5 H (C_6H_5).

2-(η⁶-Phenyltricarbonylchromium)indan-1,3-dione (**8a**).

Method A. Prepared in 90% yield by hydrolysis of 3-methoxy-2-(η⁶-phenyltricarbonylchromium)-2-inden-1-one (**15d**) (time of hydrolysis 5 min) and was identical with the material obtained by rearrangement of 3-(η⁶-benzylidenetricarbonylchromium)phthalide (**7a**) (see above).

Method B. Prepared in 90% yield by hydrolysis of 1,3-bis(ethylenedioxy)-2-(η⁶-phenyltricarbonylchromium)indan (**21**) (time of hydrolysis 1.45 h); identical with the product prepared from **15d** (*vide supra*).

Alkylation of 2-Alkyl(η⁶-indan-1,3-dione)tricarbonylchromium. General Procedure

Potassium carbonate (830 mg, 6 mmol) was added to a solution of the appropriate starting compound (0.3 mmol) in dry acetone (15 ml). The mixture was set aside at room temperature and the reaction course was followed by TLC. After no starting material was observed, the mixture was poured into water and the product was extracted into diethyl ether. The ethereal solution was washed with water and dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to flash chromatography on an SiO_2 column in isohexane–ethyl acetate.

2-Ethyl-2-methyl(η⁶-indan-1,3-dione)tricarbonylchromium (**2a**). Prepared in 40% yield by alkylation of 2-methyl(η⁶-indan-1,3-dione)tricarbonylchromium (**17a**) with ethyl iodide; red crystals, m.p. 78–79 °C, identical with the product of complexation of 2-ethyl-2-methylindan-1,3-dione (**1**). Analytical and NMR data are given on p. 489. The second product isolated was 3-ethoxy-2-methyl(η⁶-2-inden-1-one)tricarbonylchromium (**18**) (8%); red crystals, m.p. 137 °C. For $C_{15}H_{12}CrO_5$ (324.2) calculated: 55.60% C, 3.73% H; found: 55.87% C, 3.83% H. ^{1}H NMR spectrum: 1.45 t, 3 H (CH_3); 1.99 s, 3 H (CH_3); 4.52 q, 2 H (CH_2); 5.32 m, 1 H ($C_6H_4Cr(CO)_3$); 5.55 d, 2 H, J = 3 ($C_6H_4Cr(CO)_3$); 6.00 d, 1 H, J = 6 ($C_6H_4Cr(CO)_3$).

2-Ethyl-2-methyl(η⁶-indan-1,3-dione)tricarbonylchromium (**2b**). Prepared by alkylation of 2-ethyl(η⁶-indan-1,3-dione)tricarbonylchromium (**17b**) with methyl iodide in 50% yield; red crystals, m.p. 121–123 °C, identical with the product of complexation of 2-ethyl-2-methylindan-1,3-dione (**1**).

Our thanks are due to Dr E. Solcaniova and Dr E. Greiplova and their staff for ^{1}H NMR measurements and microanalyses, respectively. We thank also Slovak Ministry of Education (Grant No. 1/1443/94) for the financial support.

REFERENCES

1. Hrnciar P., Kovalcik V.: Chem. Zvesti *16*, 200 (1962).
2. Hrnciar P., Lacova M., Kovalcik V.: Pharmazie *23*, 499 (1969).
3. Nauba W. Th., Rekker R. F.: *Pharmachemistry of 1,3-Indandiones*. Elsevier, Amsterdam 1981.
4. Walter W.: Pes. Control *25*, 16 (1957).
5. Hrnciar P., Szemes F., Livar M., Perjessy A.: Collect. Czech. Chem. Commun. *38*, 417 (1973).
6. Hrnciar P., Melichercik M.: Collect. Czech. Chem. Commun. *38*, 1200 (1973).
7. Hrnciar P., Kolacan A.: Collect. Czech. Chem. Commun. *41*, 2911 (1976).
8. Hudecek M., Toma S.: J. Organomet. Chem. *393*, 315 (1990).

9. Wislicenus W.: Ber. Dtsch. Chem. Ges. *20*, 589 (1887).
10. Vogel A.: *Textbook of Practical Organic Chemistry*, 4th ed., p. 861. Longman, London 1978.
11. Struharik M., Hrnciar P.: Chem. Papers *39*, 391 (1985).
12. Mowry D. T., Ringwall E. L., Renell M.: J. Am. Chem. Soc. *71*, 120 (1949).
13. Furdik M., Lacova M., Livar M., Hrivnak J.: Chem. Zvesti *20*, 834 (1966).
14. Hrnciar P.: Chem. Zvesti *14*, 119 (1960).
15. Hrnciar P., Ertl P., Hrnciar P., Toma S.: J. Organomet. Chem. *464*, 65 (1994).
16. Cameron A. F. B., Hunt J. S., Oughton J. W., Wilkinson P. A., Wilson B. H.: J. Chem. Soc. *1953*, 3864.
17. Ionescu J.: Bull. Soc. Chim. Fr. *47*, 210 (1930).
18. Thurkauf A., Jacobson A. E., Rice K. C.: Synthesis *1988*, 233.
19. Cowton E. L. M., Gibson (nee Thomas) S. E., Schneider M. J., Smith M. H.: J. Chem. Soc., Perkin Trans. 1 *1995*, 2077.
20. Sakane K., Tsuji Y. O., Yonoto E.: Bull. Chem. Soc. Jpn. *47*, 2410 (1974).
21. Besancon J., Top S., Tirouflet J., Gantheron B., Dusausoy Y.: J. Organomet. Chem. *94*, 35 (1975).