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ELECTROCHEMICAL REDUCTIVE ACYLATION OF (η^6-arene)$Cr(CO)_3$ COMPLEXES AND (benzophenone)$[Cr(CO)_3]_2$

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Summary

The electrochemical reductive acylation of (benzophenone)$Cr(CO)_3$ and (benzophenone)$[Cr(CO)_3]_2$ has been performed in DMF, by electrochemical reduction of complexed ketones in the presence of acetic and benzoic anhydride in excess. Three complexed benzhydryl esters $ArCH(OCOR)PhCr(CO)_3$ (Ar = Ph, R = Me; Ar = $PhCr(CO)_3$, R = Me; Ar = $PhCr(CO)_3$, R = Ph) were obtained in 46–57.5% yields after purification. Electrochemical reduction of (diphenylmethane)$Cr(CO)_3$ in the presence of acetic anhydride in excess leads to *m*-benzyl acetophenone.

Introduction

There are many examples in the literature of electrochemical reductive acylation of unsaturated compounds. Substrates such as ketones, imines, olefins, aromatic and heteroaromatic compounds as well as nitro, nitroso and azo derivatives have been reduced electrochemically in aprotic solvents in the presence of acid anhydrides or acid chlorides [1–6].

Electrochemical reductive acylation of the $Cr(CO)_3$(η^6-arene) complexes (**1**) has not been described previously. In addition to the possible use of the electrochemical method to give acylated chromium complexes, which can be decomposed by thermal, chemical [7] or electrochemical means [8–12], at least two more advantages can be envisaged. The first is related to the electron-withdrawing effect of the $Cr(CO)_3$ group which facilitates the electrochemical reduction of the arene ligand contained in **1**. The electrochemical reductive acylation of the ligand in the complexed form can thus be performed with certain acid anhydrides whose electrochemical reduction precedes before that of the free ligand. Furthermore, arenes such as benzene, which are electrochemically inactive in the range of potentials available in aprotic media, can become reducible when complexed, and therefore they can be acylated electrochemically.

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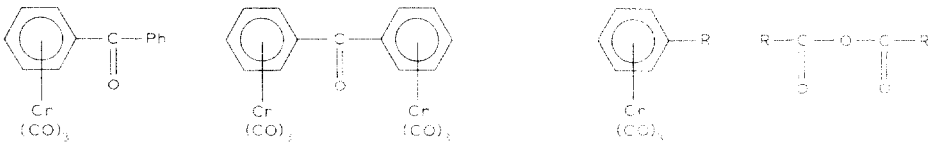
To illustrate these advantages, we describe below the electrochemical behaviour of the complexes **2**–**4** in the presence of acetic (**5a**) or benzoic (**5b**) anhydride as acylating agent. All the electrochemical experiments were carried out in DMF, at a mercury cathode, with an aqueous saturated calomel electrode (SCE) as reference electrode.



Results and discussion

The electrochemical behaviour of benzophenone(chromiumtricarbonyl) (**2**) in DMF has been previously reported [13]. In polarography, two successive one-electron steps were observed (Table 1), the first leading to the reversible formation of a radical anion (Fig. 1) of moderate stability, as revealed by controlled potential electrolysis [13]. The electrochemical reduction of the dicomplexed ketone **3** occurred in two reversible one-electron steps, as shown by cyclic voltammetry (Fig. 1). The electrochemical reduction of benzene(chromiumcarbonyl) (**4a**) and its methyl-substituted derivatives in aprotic media has been shown to take place in an overall 2-electron process [14–16], with formation of a highly reactive dianion in most cases [14–15]. In DMF, the 2-electron reduction peak of **4a** was observed with $E_{p,c} = 2.44$ V in cyclic voltammetry (peak C of Fig. 2) and was accompanied by an anodic peak C′ with $E_{p,a} = 1.84$ V. The anodic peak tended to disappear at a slow potential scan rate, v. For instance, if $i_{p,a}$ an $i_{p,c}$ are used to denote the peak currents of C and C′, the ratio $i_{p,a}/i_{p,c}$ decreased from 0.27 when v 1 V s^{-1} to 0.125 when v 0.1 V s^{-1}. The electrochemical behaviour of **4b** was very similar (peaks D and D′ of Fig. 2). The

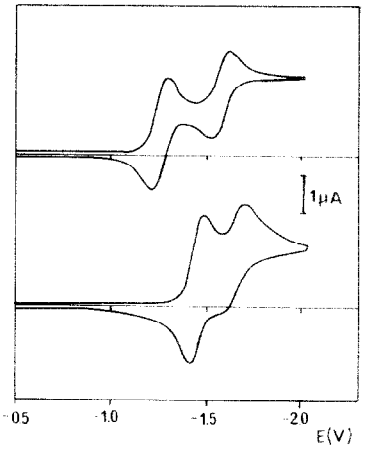


Fig. 1. Cyclic voltammograms of **2** (1 m*M*) and **3** (1 m*M*) (above curve) at 0.1 V s^{-1}.

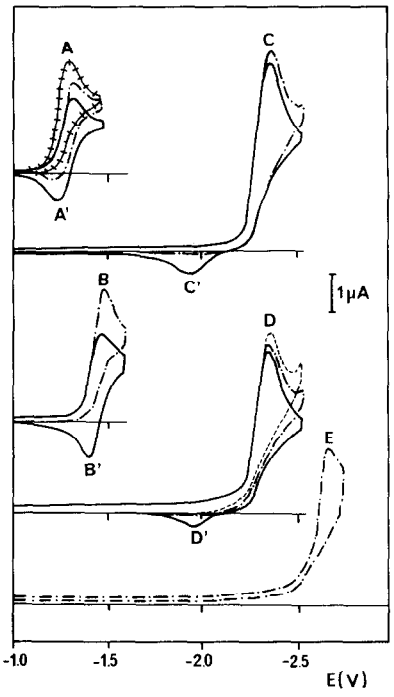


Fig. 2. Modification of the cyclic voltammograms of **3** (peaks A,A'), **2** (peaks B,B'), **4a** (peaks C,C') and **4b** (peaks D,D') upon addition of **5a** at concentrations (mM): (———) 0; (·–·–·) 1; (- - - - -) 3; (+++) 6. Curve E corresponds to **5a** (1 mM) alone. The concentration of **3**, **4** is 1 mM and the scan rate 0.1 V s^{-1}.

peak potentials $E_{p,c}$ and $E_{p,a}$ were identical, but the ratio $i_{p,a}/i_{p,c}$ was slightly lower for a given scan rate v.

The acylating agents **5a** and **5b** were irreversibly reduced with $E_{p,c}$ −2.66 and −1.72 V, respectively (peaks E of Fig. 2 and C of Fig. 3). Thus, the reductive acetylation of the complexes **2**–**4** could be investigated, as well as the reductive benzoylation of the complexed benzophenones **2** and **3**. It must be pointed out that a comparable reductive benzoylation of free benzophenone could not be carried out because the electroreduction of **5b** occurs before that of the free ketone (Table 1).

Addition of acetic anhydride (**5a**) to the complexed substrates **2**–**4** was accompanied by the disappearance of the anodic peak and by a slight increase of the cathodic

TABLE 1

HALF-WAVE POTENTIALS OF THE TWO REDUCTION WAVES OF BENZOPHENONE FREE AND COMPLEXED WITH $Cr(CO)_3$

	I $-E_{1/2}$ (V)	II $-E_{1/2}$ (V)
Ph_2CO	1.78 [a]	2.37 [a]
$(Ph_2CO)Cr(CO)_3$	1.45 [a]	1.72 [a]
$(Ph_2CO)(Cr(CO)_3)_2$	1.27	1.59

[a] See ref. 13.

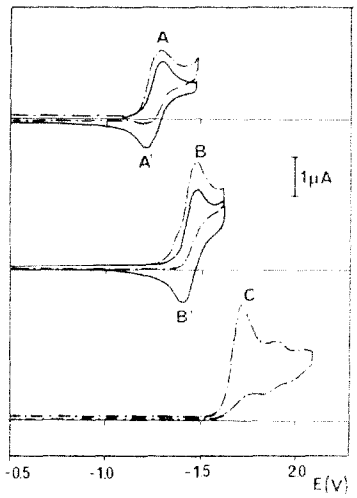
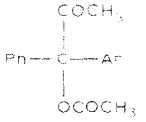


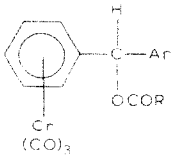
Fig. 3. Modification of the cyclic voltammograms of **3** (peaks A,A') and **2** (peaks B,B') upon addition of **5b** (1 m*M*). Curve C corresponds to **5b** (1 m*M*) alone.

current in the case of **2** and **3** (Fig. 2). Identical behaviour is observed for **2** and **3** when benzoic anhydride (**5b**) was added (Fig. 3).

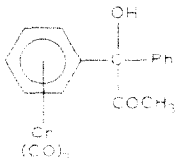
Large-scale electrolyses of **2** and **3** were carried out in the presence of acetic anhydride (**5a**) and of **3** with **5b** in excess. The acylated compounds which were isolated and their yields after purification by column chromatography are shown in Table 2. Owing to the moderate stability in DMF of the dicomplex **3**, significant amounts of **2** were isolated after electrolysis. At the potentials applied during electrolysis of **3** in the presence of **5a** and **5b**, complex **2** was not reduced. Similarly, **7b** was not very stable in DMF, where it decomposed to **7a**.



(**6a**: Ar = Ph;
6b: Ar = $(C_6H_5)Cr(CO)_3$)



(**7a**: Ar = Ph, R = CH_3;
7b: Ar = $(C_6H_5)Cr(CO)_3$, R = CH_3;
7c: Ar = $(C_6H_5)Cr(CO)_3$, R = Ph)



(**8**)

The results of Table 2 show that whereas free benzophenone was exclusively diacylated, with its complex mono O-acylation was favoured. In the case of the dicomplexed ketone **3**, the esters **7b** and **7c** were thus exclusively obtained. The electron-withdrawing effect of both $Cr(CO)_3$ groups greatly lowers the nucleophilic ability of the anion **9**, which is protonated during treatment after electrolysis.

$$Ar_2C{=}O \overset{+e}{\rightleftharpoons} Ar_2\dot{C}O^- \overset{+5}{\rightarrow} Ar_2\dot{C}OCOR + RCOO$$

$$Ar_2\dot{C}OCOR \overset{-e}{\rightarrow} Ar_2\bar{C}OCOR \qquad (Ar = C_6H_5Cr(CO)_3)$$

(**9**)

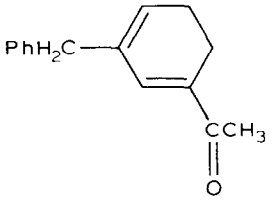
TABLE 2

ELECTROCHEMICAL REDUCTION OF BENZOPHENONE FREE AND COMPLEXED IN THE PRESENCE OF AN ACID ANHYDRIDE IN EXCESS

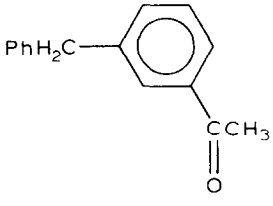
Ketone (mmol)	Acid anhydride (equiv)	n	Acylated compounds (% yield)
benzophenone(50) [a]	**5a** (8)	not indicated	**6a** (78)
2 (2)	**5a** (12.5)	1.82	**6b** (3)
			7a (57.5)
			8 (8.5)
3 (1)	**5a** (5)	1.37	**7a** (5)
			7b (55)
3 (1)	**5b** (2.5)	1.89	**7c** (46)

[a] See ref. 1.

A large scale electrolysis of (diphenylmethane)$Cr(CO)_3$ (**4b**) in the presence of an excess of acetic anhydride was carried out, and stopped after consumption of 2 F. It gave an intermediate unstable benzyldihydroacetophenone, to which structure **10** is tentatively assigned, and which was rapidly transformed into *m*-benzylacetophenone **11** [18]. The unstable compound was characterized by a conjugated carbonyl group at 1658 cm^{-1}, a methylene group at 3.45 ppm adjacent to an olefinic bond and two single protons at 5.80–6.20 (massif) and 6.7 ppm (singulet).



(10)



(11)

A large amount of unreacted **4b** was isolated after electrolysis. Integration of the ^1H NMR spectrum of the crude product of electrolysis indicated that it contained **4b** (59%) traces of diphenylmethane and **10** + **11** (29%). The formation of the free arenes **10** and **11** shows that the electrochemical reductive acetylation of **4b** is accompanied by decomplexation. However, the results do not allow us to decide whether the dianionic species **12** or its decomposition product **P**, to which is assigned the anodic peak D′ in cyclic voltammetry (Fig. 2), is the reacting species involved in the acylation process.

$$PhCH_2PhCr(CO)_3 \xrightarrow{+2e} [PhCH_2PhCr(CO)_3)]^2 \xrightarrow{dec.} \mathbf{P}$$

(12)

The low current efficiency of the process (29% for a 2-electron process) suggests that at the potential applied during electrolysis a concomitant electrochemical reduction of **5a** occurs (cf. Fig. 2).

Conclusion

Electrochemical reduction of complexed benzophenone in the presence of acid anhydride provides a route to the corresponding benzhydryl ester complexes. The

one-step electrochemical synthesis of *m*-benzylacetophenone is particularly attractive, since Friedel–Crafts acetylation of diphenylmethane leads exclusively to the *p*-acetylated derivatives [19–20].

Experimental

The complexes **2**, **3** and **4b** were prepared as described in ref 17. Benzene(chromiumtricarbonyl) was purchased from Strem Chemicals. DMF of analytical grade was carefully dried on neutral alumina. Tetrabutylammonium salts (Bu_4NPF_6 and Bu_4NBF_4) were crystallized from ethanol.

Elemental analyses were performed by Service Central d'Analyses, CNRS, Lyon. Spectra were recorded by means of the following instruments: infrared, Perkin–Elmer 580B; ^1H NMR, Jeol FX 100; mass spectra, Finnigan 3002.

Cyclic voltammograms at a stationary hanging mercury drop electrode were obtained with a Tacussel UAP 4 unit and a GSTP function generator and were recorded on an Ifelec 2025-CX-Y recorder. An Amel 552 potentiostat and a Tacussel IG5-N integrator were used in preparative electrolysis. All the potentials are relative to the aqueous saturated calomel electrode (SCE).

Large-scale electrolyses were carried out in a H-type cell filled with DMF containing 0.1 *M* Bu_4NPF_6 or Bu_4NBF_4. The cathode was a mercury pool and the anode a Pt grid. The catholyte (60 ml) was deaerated with argon prior to the introduction of the complexed substrate and the acylating agent. The electrolyses were performed under argon at controlled potentials and were stopped when the Faradaic current became negligible. The catholyte was diluted with water, then NaOH 1 *M* in water was added dropwise until pH 8. The electrolysis products were extracted with diethyl ether. The etheral solution was dried, the solvent was removed, and the crude product was subjected to column chromatography.

Electroreduction of **2** *(2 mmol) in the presence of* **5a** *(12.5 equivalents)*

The potential changed from −1.31 to −1.50 V during electrolysis; $n = 1.82$. The crude product (0.628 g) was separated by column chromatography with a 1/1 diethyl ether/hexane mixture as eluant. The compounds were isolated in the following order: **7a** (57.5%), **6b** (3%), **2** (traces), **8** (8.5%).

*(Benzhydryl acetate)tricarbonylchromium (***7a***)*

Yellow needles, m.p. 106°C (from Et_2O/hexane). ^1H NMR ($CDCl_3$, TMS), δ (ppm) 2.18 (s, 3H, CH_3), 5.00–5.60 (mf, 5H, complexed phenyl), 6.51 (s, H, CH), 7.38 (s, 5H, C_6H_5); MS: *m/e* 362 (15, M^+), 278 (100, $M - 3CO$); IR (KBr) ν (cm^{-1}) 1965 and 1888 (C≡O), 1745 (O–C=O). Anal. Found: C, 59.70; H, 3.89; Cr 11.81. $C_{18}H_{14}O_5Cr$ calcd.: C, 59.67; H, 3.87; Cr, 14.36%.

*(1,1-Diphenyl-1-acetoxy-2-propanone)tricarbonylchromium (***6b***)*

Because of the low yield this compound was identified only by its ^1H NMR, MS and IR spectra. ^1H NMR ($CDCl_3$, TMS) δ (ppm) 2.08 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 4.80–6.00 (mf, 5H, complexed phenyl), 7.20–7.70 (mf, 5H, phenyl); MS: *m/e* 404 (3, M^+), 320 (100, $M - 3CO$); IR (KBr): ν (cm^{-1}) 1965 and 1885 (C≡O), 1742 (O–C=O), 1718 (C–C=O).

*(1,1-Diphenyl-1-hydroxy-2-propanone)tricarbonylchromium (**8**)*

Yellow needles, m.p. 98–99°C (from Et_2O/hexane). ^1H NMR ($CDCl_3$, TMS). δ (ppm) 2.35 (s, 3H, CH_3), 3.80 (s, H, OH, exchangeable with D_2O), 5.00–6.10 (mf, 5H, complexed phenyl), 7.40 (s, 5H, phenyl); MS *m/e* 362 (7, M^+), 278 (100, $M-3CO$); IR (KBr): ν (cm^{-1}) 3379 (OH), 1965 and 1875 (C≡O), 1698 (C–C=O).

*Electroreduction of **3** (1 mmol) in the presence of **5a** (5 equivalents)*

The potential changed from −1.14 to −1.30 V during electrolysis; $n = 1.37$. The crude product (0.407 g) was separated by column chromatography with a 1/1 diethyl ether/hexane mixture as eluant. The compounds were eluted in the order: **7a** (5%), **2** (15%), **7b** (55%) and **3** (traces).

*(Benzhydryl acetate)bis-(tricarbonylchromium) (**7b**)*

Yellow powder, m.p. 160°C (decomp.; from Et_2O/hexane). ^1H NMR ($CDCl_3$, TMS) δ (ppm) 2.22 (s, 3H, CH_3), 5.12–5.70 (mf, 10H, 2 complexed phenyls), 6.16 (s, 1H, CH). MS: *m/e* 498 (7, M^+), 414 (4, $M-3CO$), 330 (100, $M-6CO$). IR (KBr): ν (cm^{-1}) 1968 and 1885 (C≡O), 1755 (O–C=O). Anal. Found: C, 50.41; H, 2.85; Cr, 21.04. $C_{21}H_{14}O_8Cr_2$ calcd.: C, 50.61; H, 2.81; Cr, 20.88%.

*Electroreduction of **3** (1 mmol) in the presence of **5b** (2.5 equivalents)*

The potential changed from −1.1 to −1.40 V during electrolysis; $n = 1.89$. The crude product (0.640 mg) was separated by column chromatography with a 1/1 diethyl ether/hexane mixture as eluant. The compounds were eluted in the order: **5b** (0.86 mmol), **2** (traces), **7c** (46%), **3** (traces).

*(Benzhydryl benzoate)bis-(tricarbonylchromium) (**7c**)*

Yellow powder, m.p. 160°C (decomp.; from CH_2Cl_2/hexane). ^1H NMR ($CDCl_3$, TMS) 5.15–5.83 (mf, 10H, 2 complexed phenyls), 6.45 (s, 1H, CH), 7.40–7.65 (mf, 3H, aromatic H), 8.12 (d, *J* 8 Hz, 2H, aromatic H). MS: *m/e* 560 (3, M^+), 476 (9, $M-3CO$), 392 (23, $M-3CO$), 348 (100). IR (KBr): ν cm^{-1} 1972 and 1879 (C=O), 1715 (O–C=O). Anal. Found: C, 55.76; H, 2.97; Cr, 18.48. $C_{26}H_{16}O_8Cr_2$ calcd.: C, 55.71; H, 2.86; Cr, 18.57%.

*Electroreduction of **4b** (6 mmol) in the presence of **5a** (5 equivalents)*

The electrolysis was performed at −2.4 V and stopped after consumption of 2 electrons, although the Faradaic current had fallen only from 300 to 270 mA. After the usual treatment of the catholyte, the aqueous phase was lavender blue, showing the presence of inorganic chromium species in solution. Integration of ^1H NMR of the crude product (1.546 g) revealed the presence of a large amount of unreacted **4b** (3.53 mmol, 59%), traces of diphenylmethane, and a mixture of **10** + **11** (1.76 mmol, 29%). The crude product was separated by column chromatography with a 1/9 acetone/hexane mixture as eluant; **4b** is only slightly soluble in this mixture, and so could be isolated pure in large amount by filtration. The compounds were isolated in the order: diphenylmethane, **10** + **11**, **4b**. The mixture of **10** + **11** was again subjected to column chromatography with a 1/4 diethyl ether/hexane mixture as eluant, and **11** being eluted first.

Compound **10** was too unstable for unambiguous identification. (It was quantitatively transformed into **11**.) ^1H NMR ($CDCl_3$, TMS) δ (ppm) 2.20–2.50 (mf.4H),

3.45 (broad s,2H), 5.80–6.20 (mf,1H), 6.70 (broad s,H), 7.2 (broad s,5H); IR (film) ν (cm^{-1}) 3025, 2935, 1658 (C=O), 1264.

m-Benzylacetophenone (11)

White viscous oil (18). ^1H NMR ($CDCl_3$, TMS) δ (ppm) 2.57 (s, 3H, CH_3), 4.04 (s,2H,CH_2), 7.20 (s,5H,phenyl), 7.20–7.50 (mf, 2H, aromatic H), 7.70–7.95 (mf, 2H, aromatic H); MS: m/e 210 (52, M^+), 195 (100, $M - CH_3$); IR (film): ν cm^{-1} 1681 (C=O), 783.6 (*meta*-substituted benzene).

Acknowledgements

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