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Electrochemical reductive alkylation of (benzophenone)$Cr(CO)_3$ and (benzophenone)$[Cr(CO)_3]_2$

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Abstract

The electrochemical reduction of (benzophenone)$Cr(CO)_3$ and (benzophenone)$[Cr(CO)_3]_2$ in the presence of a series of alkyl chlorides which are more difficult to reduce, has been carried out in *N,N*-dimethylformamide on a mercury pool cathode. When methyl chloride and *p*-cyanobenzyl chloride are used as alkylating agents, complexed monoalkylated ethers are exclusively obtained as substitution products, in yields ranging from 36 to 54%. Complexed alkylated alcohols are isolated as the major products when (benzophenone)$Cr(CO)_3$ is reduced in the presence of benzyl-chloride and its 2,3,5-trimethyl derivative, in 48 and 44% yields, respectively. These last results suggest the intermediate formation of a charge transfer complex between the aromatic ring of the electrophile and the complexed ketone.

Introduction

Synthesis of chromium tricarbonyl complexes of the ligands **1**–**3** has been carried out in a few cases [1–5]. Mono- and dicomplexed ethers **4a,b** and **5b** have been synthesized through carbenium ion salts generated from the corresponding complexed benzhydrols [1–3]. Alcohols of type **6** have been prepared by addition of Grignard reagents to (benzophenone)$Cr(CO)_3$ [4]. A multistep synthesis of the dialkylated ether **7a** involved the intermediate formation of the alcohol **6a** and the corresponding carbenium ion salt [5].

Electrochemical reduction of benzophenone in the presence of an alkyl halide RX which is more difficult to reduce has given ethers of types **1** and **3**, and alcohols of type **2** [6,7]. These results suggested that a possible single-step method of preparing complexes of types **4**–**7** would be provided by cathodic reductive alkylation of benzophenone complexed by one or two $Cr(CO)_3$ groups. We have shown previously [8] that the alcohol **6d** can be synthesized regioselectively by cathodic

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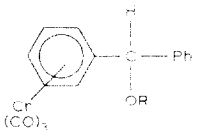
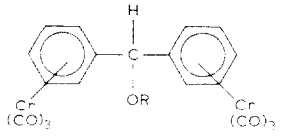
(1)

(2)

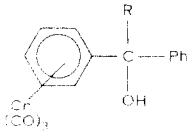
(3)



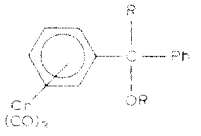
(4a, R = CH_3;
4b, R = C_2H_5;
4c, R = CH_2–C$_6$H$_4$–CN)



(5a, R = CH_3;
5b, R = C_2H_5)

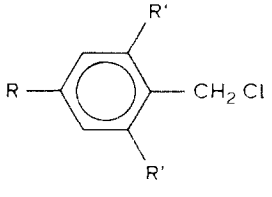


(6a, R = CH_3;
6b, R = CH_2Ph;
6c, R = CH_2–C$_6$H$_3$Me$_2$;
6d, R = $CH_2CH{=}CH_2$)

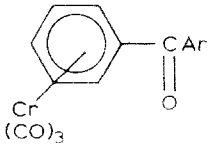


(7a, R = CH_3;
7b, R = CH_2Ph;
7c, R = CH_2–C$_6$H$_3$Me$_2$)

reduction of (benzophenone)$Cr(CO)_3$ (**9a**) in the presence of 1,3-dibromopropane. We describe below the electrochemical reduction of benzophenone complexed by one or two $Cr(CO)_3$ groups, in the presence of an excess of methyl chloride or of benzyl chloride (**8a**) or its substituted derivatives **8b,c**. The electrolyses were performed in *N,N*-dimethylformamide (DMF) on a mercury pool cathode. We found that the complexed ethers **4**, **5** were selectively formed in the presence of methyl chloride and **8b**. Conversely, alkylated alcohols **6** were predominantly formed in the presence of benzyl chloride (**8a**) and its trimethylated derivative **8c**; the mode of formation of these alcohols is considered.



(**8a**, R = R' = H;
8b, R = CN, R' = H;
8c, R = R' = CH_3)



(**9a**, Ar = Ph;
9b, Ar = $(C_6H_5)Cr(CO)_3$)

Results

At the potentials at which the radical anions of (benzophenone)$Cr(CO)_3$ (**9a**) and (benzophenone)$[Cr(CO)_3]_2$ (**9b**) were generated (their redox potentials are -1.45 V [9] and -1.27 V [10], respectively), the electrophiles were not reduced because their reduction started beyond -2 V, except in the case of **8b**. In cyclic voltammetry at a hanging mercury drop electrode (HMDE), the peak potential corresponding to the first reduction step of this compound was observed at -1.78 V. On the time-scale of the cyclic voltammetric experiments, the radical anions of (benzophenone)$Cr(CO)_3$ did not react with the electrophiles used, except **8b**, since no modification of the voltammograms was observed when the electrophiles were added. In the presence of the nitrile derivative **8b**, the cathodic peak current of the complexed ketone **9a** was doubled whereas the anodic peak was suppressed. Similarly, the radical anion of the dicomplexed ketone **9b** did not react with the electrophiles. During large-scale electrolysis at potentials corresponding to the first reduction step of the complexed ketones, reductive alkylation took place in all cases, as shown in Table 1. In most of the experiments the electrolyses were stopped after total depletion of the Faradaic current. (Benzophenone)$Cr(CO)_3$ (**9a**) was moderately stable in DMF since some parent ketone was isolated in all experiments (see the Experimental section). The dicomplexed ketone **9b** was even more unstable, and so **9a** as well as the parent ketone were liberated.

From the results summarized in Table 1, the following conclusions can be drawn. *O*-Alkylation of the carbonyl function proceeded regioselectively in the presence of methyl chloride and **8b**, and so the monoalkylated ether **4a** [1], **4c** and **5a** could be isolated in 54, 56 and 36% yields respectively (electrolyses no. 1–3). The relative instability in DMF of both the mono- and dicomplexed ketones was mainly responsible for these moderate yields. When benzyl chloride (**8a**) and its trimethylated derivative **8c** were used as alkylating agents, quite different results were obtained; no ether of type **4** was formed, and the complexed alcohols **6b** and **6c** were isolated as the major products together with some dialkylated ethers **7b** and **7c** (electrolyses no. 4 and 5).

Table 1

Electrochemical reduction of ketones **9a** and **9b** in the presence of an excess of alkylating agent

Electrolysis no.	Ketone (mmol)	Alkylating agent (equiv.)	n [a]	Alkylated compounds		
				O-alkylated (% yield [b])	*C*-alkylated (% yield [b])	*O*- and *C*-alkylated (% yield [b])
1	**9a** (2)	CH_3Cl (sat)	1.43 [c]	**4a** (54 [d])		
2	**9b** (1)	CH_3Cl (sat)	1.46 [c]	**5a** (36 [d])		
3	**9a** (2)	**8b** (2.5)	2.01	**4c** (66)		
4	**9a** (2)	**8a** (2.5)	2.03		**6b** (48)	**7b** (26)
5	**9a** (1.4)	**8c** (2.5)	2.80		**6c** (44)	**7c** (24)

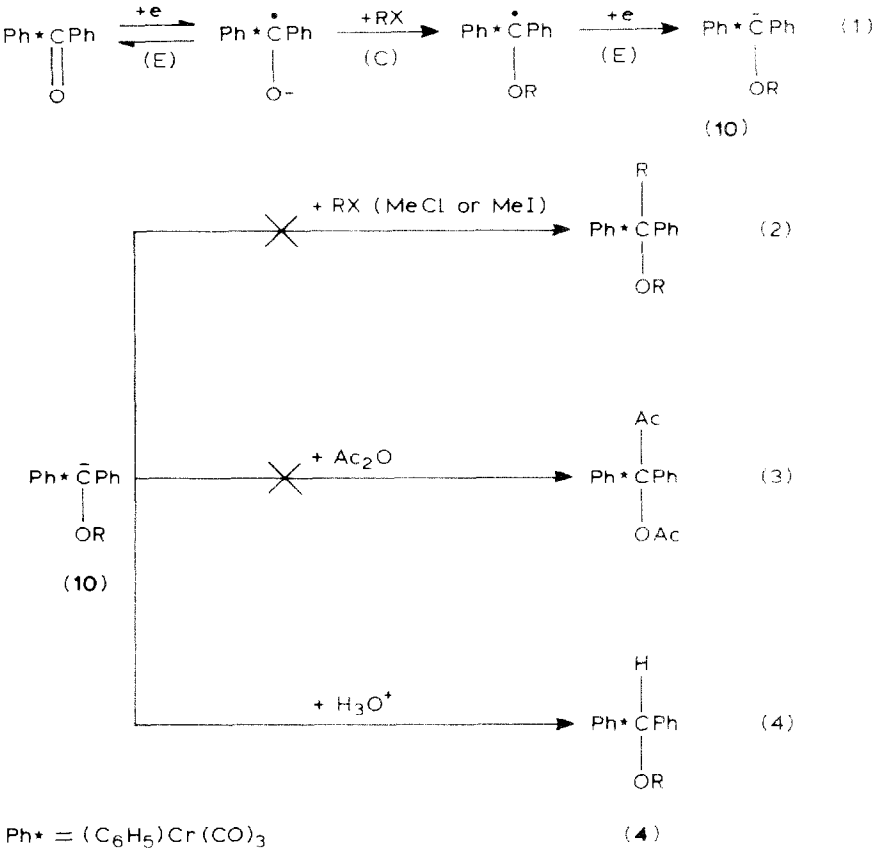
[a] Electron equivalents consumed per mole of ketone. [b] After purification by column chromatography. [c] Partial reduction of the ketone. [d] After taking account of the partial reduction of the ketone.

Discussion

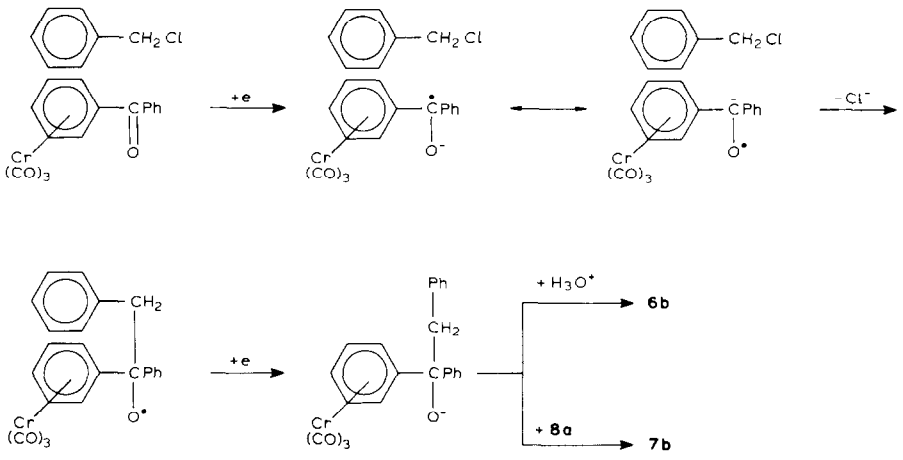
The exclusive formation of the complexed ether **4a** and **4c** during the reduction of the ketone **9a** in the presence of methyl chloride or **8a**, can be ascribed to the intermediate formation of an *O*-alkylated anion **10**, through an ECE substitution process (Scheme 1, eq. 1). This anion must possess very weak nucleophilic properties, since all attempts at its alkylation (eq. 2) or acetylation (eq. 3) failed (see the Experimental section). It would be protonated (eq. 4) during treatment of the cathodic solution.

The same considerations account for the exclusive formation of **5a**. The reductive acylation of **9a** and **9b** gave similar results, *O*-acylation occurring exclusively [10].

In the electrolyses carried out in the presence of benzyl chloride (**8a**) or its trimethylated derivative **8c**, the absence of *O*-alkylated complexes of type **4** and the formation of alcohols **6** as major compounds suggest the intermediate formation of a charge transfer complex between the aromatic ring of the electrophile **8a** or **8c** and the complexed ketone **9a** (Scheme 2 in the case of **8a**). Complex formation between benzene and (η^6-arene)Cr(CO)$_3$ has been previously shown by ^{1}H NMR spec-



Scheme 1



Scheme 2

troscopy (for a review see ref. 11 and the references included in it). It would explain the formation of an alcohol **6** as major compound and the competitive formation of a dialkylated complex **7**.

Experimental

(Benzophenone)$Cr(CO)_3$ and (benzophenone)$[Cr(CO)_3]_2$ were prepared as described in ref. 12. Except for **8b**, the electrophiles are commercially available. The nitrile **8b** was prepared from 4-cyanobenzyl bromide and an excess of acetyl chloride in boiling DMF for 2 h. The mixture was allowed to cool and NaOH 10% in water was added until the mixture was made alkaline (pH 12). Compound **8b** was extracted with diethyl ether and purified by recrystallization. Analytical grade DMF was carefully dried over neutral alumina before use.

Elemental analyses were performed by Service Central d'Analyses, CNRS, Lyon. Spectra were recorded with the following instruments: infrared, Perkin–Elmer 580B (ν (cm^{-1}) in KBr); ^1H NMR, JEOL, FX 100 (δ(ppm) $CDCl_3$/TMS); 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 an 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 before the introduction of the complexed substrate and the alkylating agent. The electrolyses were performed under argon at controlled potentials corresponding to -1.40 ± 0.10 V and 1.28 ± 0.02 V for (benzophenone)$Cr(CO)_3$ and (benzophenone)$[Cr(CO)_3]_2$, respectively. If not otherwise specified in Table 1, the electrolyses were stopped when the Faradaic current became negligible after total consumption of the ketone.

The catholyte was diluted with water and the electrolysis products were extracted with diethyl ether. The ethereal solution was dried, the solvent was removed, and the compounds were purified by recrystallization (electrolysis no. 3) or by column chromatography of the crude product with 5/5 diethyl ether/hexane (electrolyses no. 1, 2, 4) or 1/9 acetone/hexane (electrolysis no. 5) as eluant. Partial decomposition of the ketone **9a** took place during electrolysis, since benzophenone was obtained in yields of 5 to 30%. Similarly, benzophenone and **9a** were isolated when **9b** was reduced in the presence of methyl chloride (electrolysis no. 2). The composition of the crude product was not changed when the reduction of **9a** in the presence of methyl chloride (electrolysis no. 1) was followed by the addition of methyl iodide or acetic anhydride in excess. The physical and spectroscopic properties of the new complexes isolated are given below.

*(Methoxy-diphenylmethane)bis(tricarbonylchromium) (**5a**)*

Yellow crystals, m.p. 142°C (from Et_2O/hexane). ^1H NMR 3.64 (s, 3H, CH_3), 4.45 (s, 1H, CH), 5.15–5.70 (m, 10H, two complexed phenyls). IR: 1955 and 1878 (C≡O). Anal. Found: C, 50.50; H, 2.91; Cr, 21.67. $C_{20}H_{14}Cr_2O_7$ calc: C, 51.06; H, 2.98; Cr, 22.13%.

*(Phenyl(p-cyanobenzyloxy)(η^6-phenyl)methane)tricarbonylchromium (**4c**)*

Yellow crystals, m.p. 193°C (from CH_2Cl_2/hexane). ^1H NMR 4.50 (s, 1H, CH), 4.85 (m, 2H, OCH_2), 5.13–5.58 (m, 5H, complexed phenyl), 5.58 (s, 1H, CH), 7.45–7.66 (m, 9H, phenyl and p-CNC_6H_4). IR 2231 (C≡N), 1962 and 1885 (C≡O). MS: m/e 433 (18, M^+), 349 (68, $M^+ - 3CO$), 165 (100). Anal. Found: C, 66.22; H, 3.61; N, 3.31; Cr, 9.74. $C_{24}H_{17}CrNO_4$ calc: C, 66.36; H, 3.68; N, 3.28; Cr, 11.98%.

*(1,2-Diphenyl-1-(η^6-phenyl)ethanol)tricarbonylchromium (**6b**)*

Yellow crystals, m.p. 161°C (from Et_2O/hexane). ^1H NMR 3.52 (d, 2H, CH_2, J_{AB} 13 Hz), 2.34 (s, 1H, OH, exchangeable with D_2O), 5.10–5.73 (m, 5H, complexed phenyl), 6.87–7.39 (m, 10H, two phenyls). IR 3533 (OH), 1972 and 1878 (C≡O). MS: m/e 410 (13, M^+), 326 (100, $M^+ - 3CO$). Anal. Found: C, 67.05; H, 4.38; Cr, 12.50. $C_{23}H_{18}CrO_4$ calc: C, 67.32; H, 4.39; Cr, 12.68%.

*(Benzyl-benzyloxy-phenyl-(η^6-phenyl)methane)tricarbonylchromium (**7b**)*

Yellow crystals, m.p. 158°C (from Et_2O/hexane). ^1H NMR 3.66 (dd, 2H, CH_2, J_{AB} 14 Hz), 4.52 (m, 2H, OCH_2), 4.67–5.53 (m, 5H, complexed phenyl), 6.88–7.76 (m, 15H, three phenyls). IR 1965 and 1880 (C≡O). MS: m/e 500 (10, M^+), 416 (96, $M^+ - 3CO$), 91 (100, $C_7H_7^+$). Anal. Found: C, 72.06; H, 4.79; N, 10.14. $C_{30}H_{24}CrO_4$ calc: C, 72.10; H, 4.80; Cr, 10.40%.

*(1-Phenyl-2-(o,o',p-trimethylphenyl)-1-(η^6-phenyl)ethanol)tricarbonylchromium (**6c**)*

Yellow crystals, m.p. 212°C (from Et_2O/hexane). ^1H NMR 1.92 (s, 6H, 2 methyls), 2.24 (s, 3H, methyl), 2.44 (s, 1H, OH, exchangeable with D_2O), 3.53 (s, 2H, CH_2), 5.03–5.70 (m, 5H, complexed phenyl), 6.79 (s, 2H, two aromatic H), 7.35 (s, 5H, phenyl). IR 3540 (OH), 1955 and 1885 (C≡O). MS: m/e 452 (11, M^+), 368 (100, $M^+ - 3CO$). Anal. Found: C, 69.29; H, 5.40; Cr, 10.10. $C_{26}H_{24}CrO_4$ calc: C, 69.03; H, 5.31; Cr, 11.50%.

((o,o',p-Trimethylbenzyl)-(o,o',p-trimethylbenzyloxy)phenyl-(η^6-phenyl)methane)tricarbonylchromium (7c)

Yellow crystals, m.p. 193°C (from CH_2Cl_2/hexane). ^1H NMR 1.75 (s, 6H, 2 methyls), 2.03 (s, 6H, 2 methyls), 2.16 (s, 3H, methyl, 2.24 (s, 3H, methyl), 3.70 (dd, 2H, CH_2, $J_{AB} = 14$ Hz), 3.94–4.25 (m, 2H, OCH_2), 5.30–5.95 (m, 5H, complexed phenyl), 6.58 (s, 2H, two aromatic H, 6.76 (s, 2H, two aromatic H), 7.30–7.54 (m, 5H, phenyl). IR 1965, 1908 and 1872 (C≡O). MS: *m/e* 584 (4, M^+), 500 (21, $M^+ - 3CO$), 133 (100, $C_{10}H_{13}^+$). Anal. Found: C, 70.35; H, 5.97; Cr, 7.40. $C_{36}H_{36}CrO_4$ calc: C, 73.95; H, 6.20; Cr, 8.89%.

Acknowledgement

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