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ELECTROSYNTHESIS OF (FLUORENONE)TRICARBONYLCHROMIUM

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Summary

(Fluorenone)tricarbonylchromium has been prepared in up to 46% yield from (fluorene)tricarbonylchromium by two electrochemical methods whose key step is the formation of the (fluorenyl)tricarbonylchromium anion which reacts further with oxygen. The first method takes advantage of the basic properties of the superoxide anion, generated electrochemically in aprotic media; this anion is able to abstract a proton from (fluorene)tricarbonylchromium. In the second method, (fluorene)tricarbonylchromium is reduced to its anion in an inert atmosphere, prior to the introduction of oxygen.

The chemical synthesis of fluorenone-$Cr(CO)_3$ (I) was first performed by thermal replacement of CO from $Cr(CO)_6$ by fluorenone (II) [1,2]. However, its yield was low (< 12%) due to the strongly electron-withdrawing carbonyl group in II, which inhibited the reaction [3a]. The synthesis of I in three steps starting from II, and including formation of fluorenone ethylene ketal, its complex-forming reaction with $Cr(CO)_6$, and cleavage of the dioxolane complex, did not improve the overall yield (7.5%) [2]. An attempt to synthesise I from fluorene–$Cr(CO)_3$ (III) and the superoxide ion (as KO_2) failed [4]; and a 45% yield of fluorenone was isolated.

We describe here two electrochemical methods which lead to interesting yields of I (up to 46% after purification). In both methods, the overall strategy involves, as a key step, the formation in *N*,*N*-dimethylformamide (DMF) by electrochemical means of the fluorenyl–$Cr(CO)_3$ anion (IV), which then reacts with oxygen to give I.

Experimental

(Fluorene)tricarbonylchromium [5] was conveniently prepared in 75% yield by refluxing fluorene (2.5 mmol) and $Cr(CO)_6$ (2.5 mmol) for 18 h in a mixture of di-n-butyl ether (100 ml) and THF (3 ml). When this thermal replacement reaction was performed in a diglyme/heptane mixture only a 22% yield of III was obtained [6].

Cyclic voltammograms at a 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 522 potentiostat and a Tacussel IG 5-N integrator were used in the coulometry and preparative electrolysis. All the potentials are referred to the aqueous saturated calomel electrode (SCE).

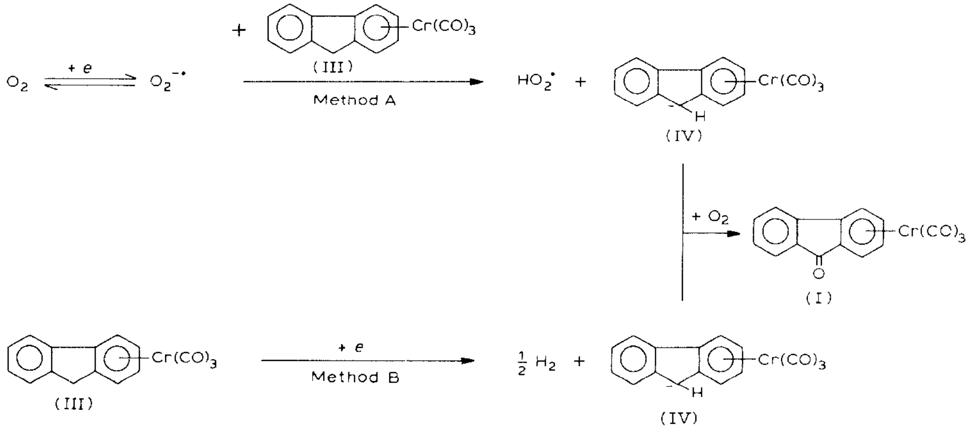
Method A. In a typical experiment, O_2^- was generated electrochemically from oxygen supplied to the cathode compartment (ca. 60 ml) of an H-cell which contained dry DMF and Bu_4NPF_6 (0.1 *M*) as supporting electrolyte. The applied potential was −1.0 V, and the working electrode was a mercury pool (ca. 13 cm^2). After consumption of 2×10^{-3} *F*, the catholyte was poured into a flask containing III, and oxygen was bubbled for 10 min in the dark. The catholyte was then diluted with water and extracted with diethyl ether. The solution was dried and the solvent removed under vacuum. The products were separated by column chromatography (on silica-gel, using hexane/dichloromethane (50%) as eluent).

Method B. The reduction of III (0.5 mmol), which was stable in DMF, was carried out at −2.05 V in the dark, in the presence of argon. After consumption of 0.9 *F*/mol, a stream of oxygen was introduced for 10 min. The products were isolated according to the procedure described in method A.

Results and discussion

Scheme 1 summarizes the two electrochemical methods which have been used.

Method A takes advantage of the basic properties of the superoxide anion O_2^-, generated electrochemically in aprotic media [7–9]. The superoxide anion O_2^- was generated in DMF by the electroreduction of oxygen, and then added to III. A mixture of the expected complexed ketone I, the uncomplexed ketone II, fluorene, V and the starting material, III, was isolated. The yields after purification by column chromatography are given in Table 1. Varying the amount of III used, showed that



SCHEME 1

the highest yield of I (46%) was obtained when $O_2^{-\cdot}$ was reacted with one equivalent of III (Experiment 1). The reaction occurred only partially when more than an equivalent of III was present (Experiment 2), whereas the formation of the parent ketone, II was favoured when an excess of O_2^{-} was used (Experiment 3).

Although the detailed mechanism of the reaction leading to I from the complexed anion IV has not been established, it can be shown that it differs from the mechanism which leads to the electrocatalytic transformation of fluorene to fluorenone in the presence of oxygen and a trace of superoxide anion generated electrochemically [7,10]. The results in Table 1 show than an equivalent of $O_2^{-\cdot}$ was consumed. On the another hand, they suggest that decomposition of some intermediate complex proceeds alongside the formation of I. In the first experiment, the amount of I is equivalent to the total amount of the free arene ligands II and V (the former probably being formed from the latter). In experiment 3, where $O_2^{-\cdot}$ is in excess, the decomposition is favoured, since the total yield of II and V is about twice that of I.

In method B, the complex III is reduced to its anion IV in an inert atmosphere, prior to the introduction of oxygen. However as shown below, a lower yield of I is obtained. The occurrence of a reductive cleavage of III is shown by cyclic voltammetry (Fig. 1). Two cathodic peaks A_1 and B_1 are observed at −2.04 and −2.64 V, and the anodic peak A_2 at −0.68 V (dotted curve of Fig. 1) is associated with A_1. Taking into account the cathodic behaviour of fluorene [11] which is reduced to hydrogen and the fluorenyl anion (in ref. 11, this anion was transformed to fluorenone by the

TABLE 1

YIELDS OF THE COMPOUNDS OBTAINED WHEN METHOD A WAS USED TO PREPARE I FROM $O_2^{-\cdot}$ (2 mmol) AND VARIOUS AMOUNTS OF III

Experiment	(III)(equiv)	Yield (%)			
		I	II	III	V
1	1	46	26	2	18
2	2	26.5	25	25	8
3	0.5	27	47	–	8.5

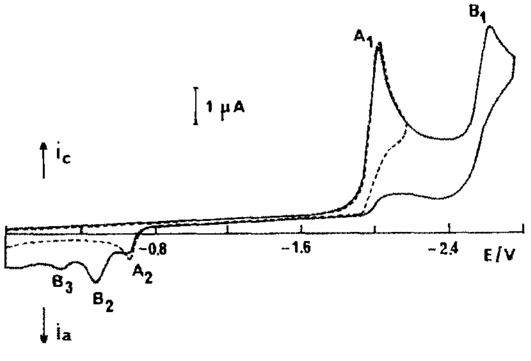


Fig. 1. Cyclic voltammogram of complex III (2 m*M*) at a hanging mercury drop electrode. The scan rate is 0.2 V s^{-1}.

addition of oxygen), it can be assumed that peak A_1 corresponds to the reductive cleavage of III, with formation of hydrogen and the anion IV. The oxidation of IV occurs at -0.68 V. By analogy with the cathodic behaviour of other (arene)tricarbonylchromium complexes [3b], peak B_1, with which are associated the anodic peaks B_2 and B_3, would correspond to the reduction of the arene ligand.

From the reduction of III, a mixture of the expected ketone I, fluorenone, fluorene and (traces of) III, was isolated. After they had been purified their yields were 23, 9, 27 and 3%, respectively. The rather high yield of fluorene can be related to the moderate stability of the anion IV in the bulk of the catholyte within the electrolysis time (about 30 min). Indeed, if the electrolysis products were extracted before the introduction of oxygen, a mixture of the complex III and the free hydrocarbon ligand V was isolated; their relative yields were 72% and 28% (determination by ^{1}H NMR spectroscopy). This shows that a partial decomposition of the electrogenerated η^6-anion IV had occurred. Its intermediate transformation into the η^5-anionic isomer [6,12,13] cannot be excluded a priori. During work-up, protonation of IV, and of its parent anion, regenerated III and V.

Method A and, in certain cases, method B should be useful for the preparation of arene and bis-arene complexes of the types $Ar^1[Cr(CO)_3]Ar^2C{=}O$ and $Ar^1[Cr(CO)_3]Ar^2[Cr(CO)_3]C{=}O$ (VI) from $Ar^1[Cr(CO)_3]Ar^2[Cr(CO)_3]CH_2$ and $Ar^1[Cr(CO)_3]Ar^2[Cr(CO)_3]CH_2$ (VII) when the last two complexes contain an acidic hydrocarbon. However any attempt to prepare (VIa) from (VIIa) ($Ar^1 = Ar^2 = C_6H_5$) failed. No proton abstraction occurred when an equivalent of O_2^- was added to the latter compound, and superoxide anion in large excess caused only partial deprotonation. In this case, in agreement with the results given above (Experiment 3 of Table 1) and with previous results [4], decomposition of the complex was favoured and only benzophenone was isolated.

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