

# Cathodic carbonylation. Synthesis of aliphatic aldehydes using an electroreductively generated iron-carbonyl anion

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**Alkyl halides are electroreductively coupled with pentacarbonyliron to generate the acyliron complexes. After hydrolytic work-up, these anionic acyl compounds produce aldehydes in good yields. The best results were obtained with the bromide as starting halide. The first step in the formation of acyliron complexes is the direct cathodic reduction of  $[\text{Fe}(\text{CO})_5]$  to the anionic species. Synthetic and mechanistic aspects of the reaction are discussed.**

A number of transition metal carbonyl anions are strong nucleophiles and react with various organic substrates by an  $\text{S}_{\text{N}}2$  process to generate alkylmetal carbonyl complexes.<sup>1</sup> The resultant 'ate' complexes undergo protolytic cleavage to produce the corresponding hydrocarbon, an overall reduction of the halide. The ease of the migratory-insertion reaction, in which alkylmetal carbonyl complexes are converted to acylmetal complexes, allows anionic metal carbonyls to be effective acylating agents for a variety of organic substrates.

The most intensively studied and synthetically developed anionic metal carbonyl species is probably disodium tetracarbonyliron,  $\text{Na}_2[\text{Fe}(\text{CO})_4]$ , developed by Cooke and Collman.<sup>1b,2</sup> Active organic halides (primary and secondary alkyl, allyl, benzyl) and tosylates react with  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  to produce anionic alkyliron complexes. In the presence of an excess of carbon monoxide or added triphenylphosphine, CO insertion takes place to form the acyl complexes, which are accessible directly by the reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  with acid halides. These anionic acyl complexes react with an acid to produce aldehydes. Oxidative cleavage of either the acyliron or alkyliron complex by oxygen or halogen produces carboxylic acid derivatives. The acyliron complex also reacts with alkyl iodides to give ketones in excellent yield.

Heck has studied another anionic transition-metal carbonyl complex which effects a variety of useful carbonylations,  $\text{Na}[\text{Co}(\text{CO})_4]$ .<sup>3</sup> Reaction with organic halides produces a neutral alkylcobalt tetracarbonyl complex, which, in the presence of carbon monoxide (1 atm), is rapidly converted to the corresponding acylcobalt tetracarbonyl. Treatment with alcohol produces the ester. Alternatively the complex can add to dienes.

Acylmetallic intermediates are also formed in phase-transfer carbonylation.<sup>4</sup> This often leads to a more efficient process, and the use of phase-transfer catalysis in organometallic chemistry is growing.

Another approach to anionic acylmetal carbonyl complexes is the reaction of the neutral metal carbonyl with carbanion donors such as an organolithium compound and a Grignard reagent.<sup>1b,5</sup> The complexes resulting from the reaction of  $[\text{Fe}(\text{CO})_5]$  with organolithium reagents are the same as those produced by the reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  with acyl halides, and are well characterized structurally. The complexes produced from carbonylnickel are quite useful in synthetic chemistry, but they are structurally less well characterized because they are unstable.

In a previous communication, we reported that alkyl halides are electroreductively coupled with  $[\text{Fe}(\text{CO})_5]$  to generate the acyliron compounds which are quenched with aqueous acid, forming aldehydes in high yields.<sup>6</sup> We also gave the

experimental details of this electroreduction.<sup>7</sup> The present paper discusses the synthetic and mechanistic aspects of this new reaction.

## Results and discussion

### Reduction potentials

Cyclic voltammograms were recorded in the cathodic direction for  $[\text{Fe}(\text{CO})_5]$  at a platinum electrode using a solution of  $0.2 \text{ mol dm}^{-3} [\text{Et}_4\text{N}]\text{ClO}_4$  in acetonitrile. The reference electrode was  $\text{Ag}/0.1 \text{ mol dm}^{-3} \text{AgNO}_3$  in acetonitrile. The results are very similar to those reported recently by other authors:<sup>8</sup> an irreversible reduction wave ( $E_p^{\text{red}} = -2.40 \text{ V vs. Ag/Ag}^+$  at a potential scan rate of  $0.1 \text{ V s}^{-1}$ ) is followed by a minor anodic peak ( $E_p^{\text{ox}} = -1.47 \text{ V}$ ). The peak current for a series of simple aliphatic halides overlapped with the background current for this solvent-electrolyte system, and addition of halide did not produce usable voltammetry curves.  $E_p$  Values were  $-2.7$  or more negative. There was no evidence of an anodic peak on reversal. The observed  $E_p$  values are collected in Table 1.

### Electroreduction

The electroreduction was carried out in a divided cell at room temperature, in acetonitrile containing tetraalkylammonium salt ( $0.24 \text{ mol dm}^{-3}$ ). Controlled-potential electroreduction (CPE) was performed with Pt plate electrodes ( $12 \text{ cm}^2$ ) until either the theoretically calculated amount of charge  $\{2 \text{ F mol}^{-1}$  of added  $[\text{Fe}(\text{CO})_5]\}$  was passed or the current dropped to approximately zero. Controlled-current electroreduction (CCE) was carried out at  $10 \text{ mA}$  with a stainless-steel plate cathode ( $18 \text{ cm}^2$ ) and a similar Pt plate anode. The cathode and anode compartments, kept under a nitrogen atmosphere, were stirred magnetically. During the reduction, evolution of CO was observed on the cathode surface. After completion of the reduction, the catholyte was treated with aqueous  $2 \text{ mol dm}^{-3} \text{HCl}$  and extracted with pentane. The pentane extract was analysed by gas-liquid chromatography (GLC). Results are shown in Table 1.

Table 1 shows that primary alkyl halides, especially bromides, afford aldehydes in high yields. The order of aldehyde yield is  $\text{RBr} > \text{RI} > \text{RCl}$ .

Since this reaction is apparently very greatly influenced by the steric environment around the leaving halide atom, 2-bromo secondary halides such as 2-bromo-pentane and -hexane give aldehydes in moderate yields whereas 3-bromo secondary halides such as 3-bromo-hexane and -heptane do not.

One of the dominant characteristics of the present reaction lies in its high reactivity for benzylic halides. Benzyl bromide was converted into dibenzyl ketone in  $\sim 50\%$  yield (based on

**Table 1** Conversion of alkyl halides into aldehydes<sup>a</sup>

RX	$E_p/V^b$	P <sup>c</sup>	E <sup>d</sup>	Electricity <sup>e</sup> (%)	Conversion (%)	Yield of RCHO <sup>f</sup> (%)
n-C <sub>5</sub> H <sub>11</sub> Cl		-2.30	T	32	15	a small amount
n-C <sub>5</sub> H <sub>11</sub> Br	~ -2.9	-2.40	B	97	77	82 (63)
n-C <sub>5</sub> H <sub>11</sub> I	~ -2.8	-2.30	I	100	97	59 (57) <sup>g</sup>
n-C <sub>6</sub> H <sub>13</sub> Cl		-2.30	T	62	13	41 (5)
n-C <sub>6</sub> H <sub>13</sub> Br	~ -2.7	-2.30	B	100	88	91 (80)
n-C <sub>6</sub> H <sub>13</sub> I		-2.30	I	94	98	55 (54) <sup>g</sup>
n-C <sub>7</sub> H <sub>15</sub> Cl		-2.30	T	52	15	2 (0.3)
n-C <sub>7</sub> H <sub>15</sub> Br		-2.30	B	100	79	80 (64)
n-C <sub>8</sub> H <sub>17</sub> Cl		-2.25	T	58	17	22 (4)
n-C <sub>8</sub> H <sub>17</sub> Br	~ -2.7	-2.20	B	100	71	85 (60)
n-C <sub>8</sub> H <sub>17</sub> I		-2.30	I	91	95	64 (61) <sup>g</sup>
n-C <sub>9</sub> H <sub>19</sub> Cl		-2.25	T	51	40	8 (3)
n-C <sub>9</sub> H <sub>19</sub> Br		-2.25	B	100	70	95 (67)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(Br)CH <sub>3</sub>	~ -2.7	-2.30	B	62	14	35 (5)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(Br)CH <sub>3</sub>	~ -2.7	-2.30	B	72	42	45 (19)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH(Br)CH <sub>3</sub>	~ -2.7	-2.30	B	70	20	75 (15)

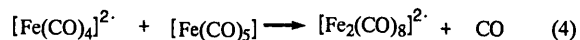
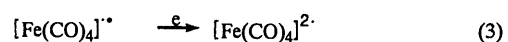
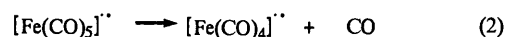
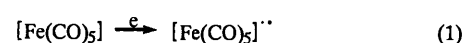
<sup>a</sup> Reactions used 2.5 mmol of RX and a slight excess of Fe(CO)<sub>5</sub>. Divided cell; Pt electrodes (2 × 3 cm); solvent, acetonitrile (50 cm<sup>3</sup> in each of the cathode and anode compartments); Ag/0.1 mol dm<sup>-3</sup> AgNO<sub>3</sub> reference; electricity, 2.0 F mol<sup>-1</sup>; proton donor used in work-up, aqueous 2 mol dm<sup>-3</sup> HCl. <sup>b</sup> Reduction peak potential, V vs. Ag/Ag<sup>+</sup>. <sup>c</sup> P: Potential for controlled-potential electroreduction. The potential was set in the region of the peak potential of [Fe(CO)<sub>5</sub>]. <sup>d</sup> Electrolyte, tetraalkylammonium salt. T: [Et<sub>4</sub>N]OTs; B: [Et<sub>4</sub>N]Br; I: [Bu<sub>4</sub>N]I. Electrolyte concentration was 0.24 mol dm<sup>-3</sup>. <sup>e</sup> Reaction was discontinued when the current dropped to about 1 mA, and the total quantity of electricity consumed was calculated based on a theoretical amount for a 2e process. <sup>f</sup> Based on halide unrecovered. The value in parentheses represents the yield based on halide used. <sup>g</sup> Symmetrical ketone. R<sub>2</sub>CO, was identified as a minor product.

benzyl bromide used) galvanostatically, together with toluene (~25%) and a small amount of dibenzyl. Potentiostatic electroreduction at -2.1 V vs. Ag/Ag<sup>+</sup> gave the ketone in 54% yield (based on benzyl bromide unrecovered), the conversion being 42%. Identical products have been produced in a different ratio by phase-transfer carbonylation.<sup>9</sup> Dibenzyl ketone can also be obtained from the reaction of the [Fe(CO)<sub>4</sub>]<sup>2-</sup> reagent with benzyl chloride in THF at room temperature in 38% yield (based on benzyl chloride used).<sup>10</sup> Treatment of the dianion with benzyl bromide at -78 °C, followed by quenching with acetic acid at 25 °C, gives toluene as the major product along with a small amount of phenylacetaldehyde.<sup>2a</sup>

### Mechanism

The desirable reaction requires a net two-electron process in agreement with the coulometry. There are essentially two different mechanisms which could account for the electrochemical carbonylation of alkyl halides. One is the possibility of a coupling of electrogenerated carbonyl-iron-complex anion with alkyl halides. [Fe(CO)<sub>5</sub>] undergoes electroreduction to produce several mono- and di-anionic species such as [Fe(CO)<sub>5</sub>]<sup>-</sup> and [Fe(CO)<sub>4</sub>]<sup>2-</sup>.<sup>11</sup> Such anions can well carbonylate organic halides (*vide infra*).<sup>1b,2,4b</sup> An alternative carbonylation route involves initial formation of aliphatic carbanions followed by combination with [Fe(CO)<sub>5</sub>].<sup>5</sup> Electroreduction of alkyl halides leads to carbanions by way of anion radicals and/or radicals.<sup>12</sup> By using the CPE technique, it is possible to distinguish between mechanisms. At the potential region adopted, alkyl halides are not discharged to any discernible extent. Consequently, the initial step in the acyliron complexes formation involves direct cathodic reduction of [Fe(CO)<sub>5</sub>] to the anionic species.

The electrochemical reduction of [Fe(CO)<sub>5</sub>] has been extensively studied.<sup>11a</sup> There was in the past some disagreement regarding the basic nature of the primary electrode process. The presently accepted mechanism is an ECE reaction sequence (Scheme 1).<sup>8,11b-d</sup> The initially generated anion radical [Fe(CO)<sub>5</sub>]<sup>-</sup> rapidly loses CO to give the coordinatively unsaturated anion radical [Fe(CO)<sub>4</sub>]<sup>-</sup>, followed by further cathodic reduction to give the stable dianion [Fe(CO)<sub>4</sub>]<sup>2-</sup>. In the absence of an electrophile such as an organic halide, the electrogenerated dianion further reacts slowly by nucleophilic



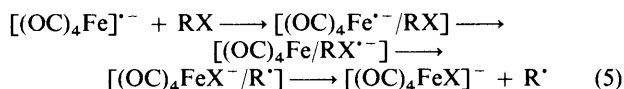
Scheme 1

substitution with unreacted [Fe(CO)<sub>5</sub>] to yield the binuclear dianion [Fe<sub>2</sub>(CO)<sub>8</sub>]<sup>2-</sup>.

The existence of an initial 19-electron anion radical [Fe(CO)<sub>5</sub>]<sup>-</sup> has been recognized in solution and in a single crystal of [Cr(CO)<sub>6</sub>] by ESR spectroscopy.<sup>13</sup> This species is best described as an acyl radical [(OC)<sub>4</sub>Fe(CO)]<sup>-</sup> in which the 19th electron resides mostly on a ligand.<sup>13b</sup> MO calculations support the acyl radical structure.<sup>14</sup> Like an organic acyl radical, this radical intermediate can be intercepted by tributyltin hydride to give a formyl complex [(OC)<sub>4</sub>Fe(CHO)]<sup>-</sup>.<sup>15</sup> An approximate lifetime was estimated to be about 10 ns,<sup>8</sup> which is probably too short to permit this radical to play a leading role under these conditions.

Observations by IR using matrix-isolation techniques and in the gas phase by ion cyclotron resonance strongly implicated involvement of the 17-electron anion radical [Fe(CO)<sub>4</sub>]<sup>-</sup> as a reaction intermediate.<sup>16</sup> The solution ESR spectrum of this anion radical was recently obtained with much effort by UV photolysis of THF-2-methyl-THF solutions of Na<sub>2</sub>[Fe<sub>2</sub>(CO)<sub>8</sub>] as a single absorption with a *g* value of 2.0486 and a temperature-dependent line width (4.7 G at -110 °C and 8.7 G at -90 °C).<sup>8,17</sup> The electron affinity was determined by photoelectron spectrometry.<sup>18</sup> Since the reduction potential of [Fe(CO)<sub>5</sub>] is much more negative ( $E_p = -2.67$  V vs. Ag/Ag<sup>+</sup> at 1 V s<sup>-1</sup>) than the standard potential for the couple [Fe(CO)<sub>4</sub>]<sup>-</sup>/[Fe(CO)<sub>4</sub>]<sup>2-</sup> ( $E^\circ = -1.89$  V),<sup>8</sup> the relevant anion radical [Fe(CO)<sub>4</sub>]<sup>-</sup> does not undergo dimerization but cathodic reduction to give the dianion [Fe(CO)<sub>4</sub>]<sup>2-</sup> when the potential was set on the reduction wave of [Fe(CO)<sub>5</sub>]. The rate constant for the dimerization of [Fe(CO)<sub>4</sub>]<sup>-</sup> has been

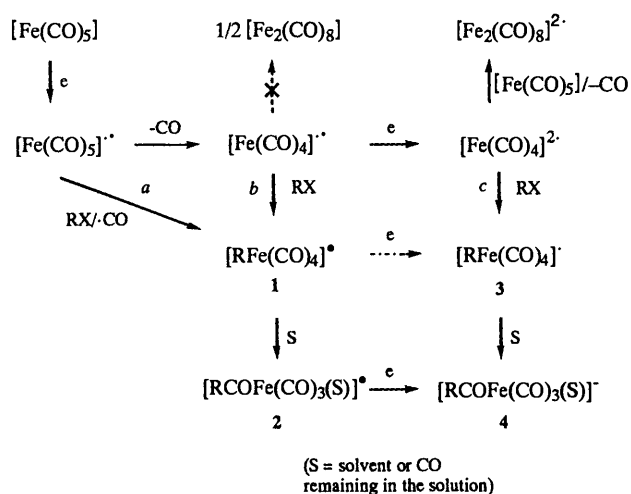
estimated at  $k \approx 5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . It is noticeable that, in the gas-phase, the reaction between  $[\text{Fe}(\text{CO})_4]^{1-}$  and haloalkanes gives the product of halogen-atom transfer:<sup>19</sup>



The rate constants for these reactions were measured and the mechanism of these (halogen-atom transfer) is thought to be electron transfer in the initially formed ion/neutral collision complex  $[(\text{OC})_4\text{Fe}^{1-}/\text{RX}]$  yielding  $[(\text{OC})_4\text{Fe}/\text{RX}^{1-}]$  followed by  $\text{X}^-$  transfer from  $\text{RX}^{1-}$  to the 16-electron metal complex  $[(\text{OC})_4\text{Fe}]$  within the collision complex to give the product  $[(\text{OC})_4\text{FeX}]^{1-}$  and  $\text{R}^{\cdot}$ . It should be noted that it is the presence of solvent which affects the course of a reaction.<sup>20</sup> Indeed, in solution organic anion radicals react with alkyl halides to capture organic moieties and release halide ions.<sup>21</sup> Accordingly, it is expected that the reaction between  $[\text{Fe}(\text{CO})_4]^{1-}$  and alkyl halides gives alkyltetracarbonyliron radicals  $[(\text{OC})_4\text{FeR}]^{\cdot}$  and halide ions.

A third candidate for reactive intermediate is the mononuclear dianion  $[\text{Fe}(\text{CO})_4]^{2-}$ . This dianion is well-known with sodium as countercation (Collman's reagent) and is a powerful nucleophile and a reducing reagent widely used in organic and organometallic chemistry.<sup>2d</sup> Alkyl halides react with this dianion to form the alkyltetracarbonyliron anion, which may be in equilibrium with the coordinatively unsaturated acyliron anion.

The aforementioned findings and precedents from other carbonylations by carbonyl metal anions lead us to the parallel electron-transfer mechanism for cathodic carbonylation of haloalkanes as shown in Scheme 2. The formation of the



Scheme 2

alkyltetracarbonyliron radical  $[\text{RFe}(\text{CO})_4]^{\cdot}$  1 may be explainable by two pathways, namely, the reaction between the initial anion radical  $[\text{Fe}(\text{CO})_5]^{1-}$  and alkyl halides followed by CO loss (path *a*), and the reaction between the subsequent anion radical  $[\text{Fe}(\text{CO})_4]^{1-}$ , formed by CO cleavage from the initial anion radical, and alkyl halides (path *b*). The resultant complex 1 undergoes migratory insertion promoted by solvent or CO remaining in the solution as a by-product of the reduction to give the solvent-substituted acyliron radical 2, which is further reduced to form a key intermediate  $[\text{RCOFe}(\text{CO})_3\text{S}]^{\cdot}$  4. The existence of acyliron radical species 2 (S = CO) has clearly been recognized by an ESR study.<sup>22</sup> A second anion radical  $[\text{Fe}(\text{CO})_4]^{1-}$  could undergo further reduction (*vide supra*) to afford tetracarbonyliron dianion  $[\text{Fe}(\text{CO})_4]^{2-}$ , which would react with alkyl halides to give alkyltetracarbonyliron anion

$[\text{RFe}(\text{CO})_4]^{1-}$  3 followed by solvent-assisted migratory insertion.

In order to gain supporting evidence for the formation of acyliron complex anion 4, present as the tetraalkylammonium salt, the solution phase IR spectrum was taken at the beginning and at the end of the reaction (R = *n*-C<sub>6</sub>H<sub>13</sub>). At the end of the reaction  $[\text{Fe}(\text{CO})_5]$  had completely disappeared, and the new bands appearing were found to be fully consistent with those quoted in literature for the acyltetracarbonyliron anion.<sup>5b,23</sup> The IR spectrum of the residue obtained after evaporation of the solvent showed a medium absorption band at  $1600 \text{ cm}^{-1}$  (RCOFe; masked in solution IR spectrum). Very similar results were observed for other alkyl bromides. This anion 4 reacts with another alkyl halide to give the ketone.

Protonation of the anion 4 by aqueous acid should lead to the intermediate acyl-hydrido iron complex  $[(\text{RCO})\text{HFe}(\text{CO})_3(\text{S})]$  which appears to immediately collapse to the aldehyde. Such an intermediate has been postulated already in the synthesis of aldehydes by protonation of anionic acyliron complexes.<sup>2a</sup>

Under these circumstances, it is instructive to comment briefly on the feasibility of using the CPE technique for studying the reaction mechanism. This technique was once used by Petit and co-workers to determine the electroactive material, either  $[\text{Fe}(\text{CO})_5]$  or the organic halide (or both).<sup>24</sup> The EEC<sub>c</sub>C<sub>p</sub>-type mechanism<sup>25</sup> was proposed in which electrogenerated inorganic anion radical and alkyl radical formed by concurrent reduction of alkyl halide combine. Their results and conclusions are in conflict with ours. They used less polar THF as solvent in an undivided cell and set the electrode potential of the working electrode at the more cathodic levels by about 0.2 V than the respective reduction potentials of  $[\text{Fe}(\text{CO})_5]$  and ethyl iodide. Acylmetallic intermediates were formed at both potentials. We suggest that their conclusions are insecure, based as they are on insufficient evidence; *viz.*, in parallel reactions, the relative yields of products at a given electrode potential depend on the values of the component currents.<sup>26</sup> When the potential of the working electrode in the reaction in question is controlled at  $-2.0 \text{ V vs. Ag/Ag}^+$  {more negative by 0.15 V than the given reduction potential of  $[\text{Fe}(\text{CO})_5]$ } the reduction of  $[\text{Fe}(\text{CO})_5]$  is not the only reaction. At the potential adopted, reduction of ethyl iodide occurs at the same time. In order to minimize the influence of the parallel reaction the cathode potential must be controlled at the  $-1.85 \text{ V}$  or more anodic potential. In the reaction with benzyl bromide, the difference between the given reduction potentials of  $[\text{Fe}(\text{CO})_5]$  and benzyl bromide is no more than 0.1 V; it is hard to determine which species is being discharged using the CPE technique.

While electrogenerated carbonyl-iron anion is an effective reagent for the conversion of primary aliphatic bromides into homologous aldehydes, secondary bromides are less satisfactory. The reaction was discontinued when the current dropped to nearly 1 mA, until then the total quantity of electricity consumed in the electroreaction was no more than 70% of the theoretically calculated amount of charge (an overall 2e process). The current efficiency for desired carbonylation reactions was 20% or so and the remainder of the current would be consumed with inorganic reaction {probably the coupling reaction of the starting  $[\text{Fe}(\text{CO})_5]$  with electrogenerated  $[\text{Fe}(\text{CO})_4]^{2-}$  [(Eqn. (4))]. The greater part of bromides was recovered. These results imply that the alkylation of the reactive carbonyl-iron complex anions by secondary bromides is fast enough to compete with the coupling reaction leading to  $[\text{Fe}_2(\text{CO})_8]^{2-}$ . The rate constant of the latter reaction in acetonitrile has been estimated at  $4.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .<sup>11c</sup>

## Conclusions

The present results show that the carbonyl-iron complex anion derived from  $[\text{Fe}(\text{CO})_5]$  is an effective reagent for the conversion of primary bromides into the corresponding aldehydes

containing an additional carbon atom. The initial step in the acyliron complex formation involves direct cathodic reduction of  $[\text{Fe}(\text{CO})_5]$  to the anionic species. This reaction is very convenient in point of the use of easily handled material when compared with the non-electrochemical procedure using a moisture-sensitive, very pyrophoric material such as organolithium or  $\text{Na}_2[\text{Fe}(\text{CO})_4]$ . The scope and limits of this new electroreduction are presently under investigation.

## Experimental

### General

IR spectra were recorded on a Shimadzu Model IR-408 spectrophotometer. GLC analysis of product mixtures was carried out on a Shimadzu Model GC-7A gas chromatograph utilizing a flame ionization detector. The columns employed for the analyses were PEG 6000, Silicone DC550, Silicone GE XF-1150 or Silicone GE SE-30.

### Materials

Halogenoalkanes were purchased.  $[\text{Fe}(\text{CO})_5]$  was used as received from Aldrich Co. The following supporting electrolytes were purchased:  $[\text{Et}_4\text{N}]\text{Br}$ ,  $[\text{Et}_4\text{N}]\text{Cl}$ ,  $[\text{Et}_4\text{N}]\text{ClO}_4$ ,  $[\text{Et}_4\text{N}]\text{OTs}$  and  $[\text{Et}_4\text{N}]\text{I}$ . Most aldehydes as reference materials and GLC internal standards were commercial samples. 2-Methyl-hexanal and -octanal were prepared by the Grignard procedure from the corresponding halides and ethyl orthoformate.<sup>27</sup>

### Cyclic voltammetry (CV)

Cyclic voltammetry was carried out using a Hokuto Denkoh Model HA-501 potentiostat in conjunction with a Hokuto Denkoh Model HB-107A function generator. Cyclic voltammograms were recorded on a Yokogawa Model 3086 X-Y recorder. The cell for cyclic voltammetry was a 20 cm<sup>3</sup> single compartment cell equipped with a gas inlet tube. The working electrode was a 1 cm platinum wire. The counterelectrode was a sheet of platinum foil. The reference electrode was a silver wire immersed in acetonitrile containing tetraethylammonium perchlorate (0.2 mol dm<sup>-3</sup>) and silver nitrate (0.1 mol dm<sup>-3</sup>). The half-cell, whose exit end was made narrower and packed with glass wool, was located in a bridge (an acetonitrile solution containing 0.2 mol dm<sup>-3</sup>  $[\text{Et}_4\text{N}]\text{ClO}_4$ ) and connected to the solution by a fine glass frit whose tip is placed close to the working electrode. All potentials are given against this reference.

A 0.2 mol dm<sup>-3</sup>  $[\text{Et}_4\text{N}]\text{ClO}_4$ -MeCN solution was employed for all voltammograms. Acetonitrile was purified by drying with calcium hydride followed by two distillations from phosphorus pentoxide and a third distillation from calcium hydride.<sup>28</sup>  $[\text{Et}_4\text{N}]\text{ClO}_4$  was purchased and dried in a vacuum oven for 2 days at 100 °C.

Cyclic voltammograms were run at  $5 \times 10^{-3}$  mol dm<sup>-3</sup> substrate concentrations.  $E_p^{\text{red}}$  Values are quoted for rates of 0.1 V s<sup>-1</sup>.

### Preparative-scale electroreduction

CPEs were performed with the same potentiostat coupled with a Hokuto Denkoh Model HF-201 digital coulometer. The reaction vessels were two-compartment H-type cells with a medium-porosity glass frit as a cell divider, equipped with gas inlet tubes. Both the catholyte and anolyte capacities were 50 cm<sup>3</sup>. For CPE, the cathode compartment contains the Ag/Ag<sup>+</sup> reference electrode prepared as mentioned above, which was separated from the bulk solution by a fine glass frit and positioned as close to the working electrode as possible. A 2 × 3 cm platinum sheet was used as working electrode. A 3 × 3 cm stainless-steel sheet cathode was used for CCE. A 3 × 3 cm platinum sheet was used as counterelectrode for all electroreactions.

Acetonitrile was distilled from phosphorus pentoxide just before use. Supporting electrolytes were dried in a vacuum oven at 100 °C and were routinely kept in a desiccator.

The catholyte was composed of acetonitrile (50 cm<sup>3</sup>), halogenoalkanes (2.5 mmol),  $[\text{Fe}(\text{CO})_5]$  (2.5 mmol) and supporting electrolyte (12 mmol). The anolyte was the same medium in the absence of the substrates and in the presence of ground anhydrous sodium thiosulfate (15 mmol). When non-halide electrolyte anions such as toluene-*p*-sulfonate ion ( $\text{OTs}^-$ ) were used, tetrabutylammonium iodide (12 mmol) was also added as an anodic depolarizer. The cathode and anode compartments, kept under a nitrogen atmosphere, were stirred magnetically. Reduction was performed until either 2 F mol<sup>-1</sup> of added  $[\text{Fe}(\text{CO})_5]$  was passed or the current dropped to approximately zero. CCE was carried out at 10 mA. During the electroreduction, CO gas evolved on the cathode surface. After completion of the reduction, the catholyte was treated with 350 cm<sup>3</sup> of aqueous 2 mol dm<sup>-3</sup> HCl and extracted with 100 cm<sup>3</sup> of pentane. The pentane extracts were washed with 100 cm<sup>3</sup> of saturated aq. sodium hydrogen carbonate. The extract was washed successively with 100 cm<sup>3</sup> of saturated aq. sodium thiosulfate and brine. The pentane extract was dried over magnesium sulfate, filtered and analysed by GLC using an internal standard. **CAUTION:**  $[\text{Fe}(\text{CO})_5]$  must be handled with caution in an efficient hood since it is toxic.

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