Original Communication

# Electrochemical study of the reaction yielding α-alkylated esters by electroreductive coupling of α-polychloroesters with triethylborane

**Sylvie Condon, Clément Comminges, Michel Troupel and Rachid Barhdadi***

Université Paris-Est Créteil, Institut de Chimie et des Matériaux Paris-Est, UMR 7182-CNRS,
Equipe Electrochimie Synthèse organique, 2 rue Henri-Dunant, 94320, Thiais, France

## ABSTRACT

Cyclic voltammetry shows that the electrochemical behavior of α-polychloroesters is modified in the presence of *triethylborane*, which highlights that the bielectronic reduction of the chloroester is accompanied by a fast chemical step, Chemical-Electrochemical (CE) or Electrochemical-Chemical (EC) mechanism. For the dichloroester $HCl_2C$-$CO_2C_{10}H_{21}$, the coupling with triethylborane competes with a proton exchange between the electrogenerated carbanion and the starting molecule itself. A second possible side reaction evidenced from the dichloromethylester $Me$-$Cl_2C$-$CO_2C_{10}H_{21}$ is an electroreductive dimerisation which is minimized by adding an excess of $Et_3B$.

**KEYWORDS:** polychloroester electroreduction, triethylborane, coupling reaction, α-alkylated esters

## 1. INTRODUCTION

In a recent paper [1], we disclosed an electrochemical alkylation reaction from α-polyhaloesters and trialkylborane using the sacrificial anode process. The cathodic reduction of gem-polyhalide compounds generates a halocarbanion which undergoes an alkyl transfer reaction from trialkylborane (Scheme 1, way 1). The method offers an interesting alternative to the reaction described by Brown *et al.* [2] in which

halocarbanions are obtained by removal of acidic hydrogen in the presence of a sterically hindered strong base B$^-$ (Scheme 1, path 2).

The reaction described in ref. [1] proceeded in Dimethylacetamide (DMAc) as the solvent, with a slight excess of triethylborane *vs.* the organic halide. The undivided electrochemical cell was fitted with a sacrificial zinc anode, and electrolyses were carried out at room temperature by supplying a constant current intensity. As presented in Scheme 2, this electrosynthetic reaction affords moderate to good results with sterically different trialkylboranes and gem-dihalide compounds [1].
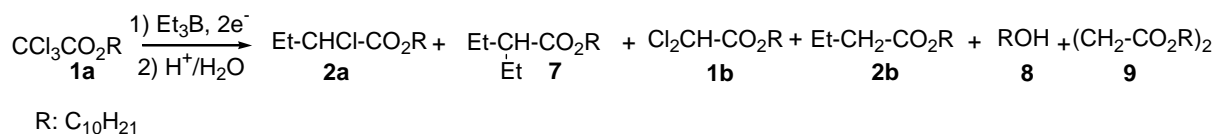
## 2. MATERIAL AND METHODS

Analyses of products were carried out by gas chromatography (Varian 3400) and gas chromatography coupled to the mass spectrometry GC-MS (Finnigan MAT GCQ).
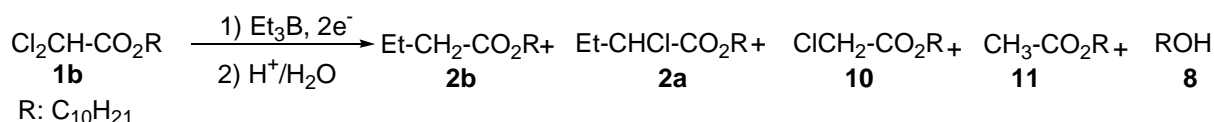
The electrochemical study presented here was carried out in the solvent Dimethylacetamide DMAc + $Bu_4NBF_4$ as supporting electrolyte with *decyl trichloroacetate* **1a**, *decyl dichloroacetate* **1b** or *decyl 2,2 dichloropropionate* **1c** as starting halocompounds and a commercial solution of *triethylborane* 1N in THF.

Electrochemical measurements were performed using a ParStat 2253 (Princeton Applied Research) potentiostat in the 3-electrodes configuration. The working microelectrode was a Pt disk (area = $3.6 \times 10^{-3}$ cm$^2$), while Pt gauze acted as the
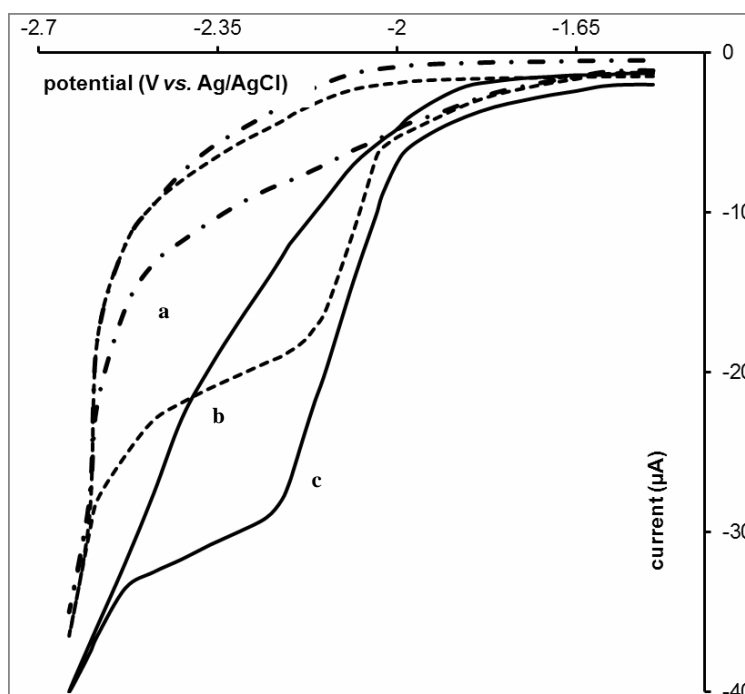
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*barhdadi@glvt-cnrs.fr

**Scheme 1**

**Scheme 2**

$$R^1CCl_2\text{-}CO_2C_{10}H_{21} \xrightarrow[\text{2) } H^+ / H_2O]{\text{1) } R_3B / 2e^-} R^1\text{-}\underset{\underset{\text{R}}{|}}{C}H\text{-}CO_2C_{10}H_{21}$$

$R^1$: H, Cl, OMe, CH$_3$

R: Et, nBu, nOct, *Sec*Bu, c(C$_6$H$_{11}$)

30 - 71%

**Scheme 3**

counter electrode. All potentials are quoted relative to the Ag/AgCl system used as reference electrode. The working electrode was polished with Emery 3/0 prior to its use, and all measurements were performed at room temperature under an argon atmosphere. The number of electrons involved in the electroreduction of Et$_3$B or chloroesters **1a,b,c** was evidenced by comparing their cathodic peak intensity to the one obtained in same experimental conditions for the classical one-electron ferrocene/ ferricinium system.

## 3. RESULTS AND DISCUSSION

The aim of our preliminary studies is purely synthetic. Here we report electrochemical data which highlight some mechanistic aspects. We want particularly to understand what side reactions give by-products and how to improve the yield in the desired product.

The formation of the expected alkylated compound from an α-polychloroester and trialkylborane is

explained according to Scheme 3. The chosen example in this scheme is the formation of decyl *2-chlorobutanoate* **2a** from *decyl trichloroacetate* **1a** and *triethylborane*. The two-electron reduction of **1a** generates the carbanionic dihalide **3,** which reacts with Et$_3$B to form the organoborate **4.** Then 1,2-migration occurs and the resulting α-chloroborylester **5** tautomerizes to alkenyloxyborane **6,** which yields **2a** after acidic work-up.

Scheme 4 illustrates that a lot of by-products are obtained in typical reactions involving *decyl trichloroacetate* (**1a**) and *triethylborane* as electrophile. Mass spectroscopy analysis evidenced the presence of the expected *decyl 2-chlorobutanoate* **2a** along with some side products: *decyl 2-ethylbutanoate* **7**, *decyl 2,2-dichloroacetate* **1b**, *decanol* **8**, *decyl butanoate* **2b** and *succinate* **9** in proportions depending on the experimental conditions.

When starting from *decyl dichloroacetate* **1b** and *triethylborane*, the main products were the two

$$CCl_3CO_2R \xrightarrow[\text{2) H}^+/\text{H}_2\text{O}]{\text{1) Et}_3\text{B, 2e}^-} Et\text{-}CHCl\text{-}CO_2R + Et\text{-}\underset{\underset{\text{Et}}{|}}{CH}\text{-}CO_2R + Cl_2CH\text{-}CO_2R + Et\text{-}CH_2\text{-}CO_2R + ROH + (CH_2\text{-}CO_2R)_2$$

**1a**     **2a**     **7**     **1b**     **2b**     **8**     **9**

R: C$_{10}$H$_{21}$

**Scheme 4**

$$Cl_2CH\text{-}CO_2R \xrightarrow[\text{2) H}^+/\text{H}_2\text{O}]{\text{1) Et}_3\text{B, 2e}^-} Et\text{-}CH_2\text{-}CO_2R + Et\text{-}CHCl\text{-}CO_2R + ClCH_2\text{-}CO_2R + CH_3\text{-}CO_2R + ROH$$

**1b**     **2b**     **2a**     **10**     **11**     **8**

R: C$_{10}$H$_{21}$

**Scheme 5**



**Fig. 1.** Cyclic voltammograms (0.1 V s$^{-1}$) in (a) DMAc + Bu$_4$NBF$_4$ 0.2 mol dm$^{-3}$: (b) +Et$_3$B 2.25 x 10$^{-2}$ mol dm$^{-3}$, (c) +Et$_3$B 4.5 x 10$^{-2}$ mol dm$^{-3}$.

alkylated compounds, **2a** and **2b**, and by-products were *decyl chloroacetate* **10**, *decyl acetate* **11**, and *decanol* **8** (Scheme 5).

Cyclic voltammograms presented in Fig. 1 show that *triethylborane* is irreversibly reduced at very low potential (about -2.2 V) before the electroreduction of the solvent/electrolyte system. The current intensities measured are compatible with a step involving 1 electron.

Fig. 2 presents the voltammograms obtained from a solution of **1a** in the absence, and then in the presence of an excess of Et$_3$B. First of all, it is evident that the electroreduction of **1a** (Fig. 2, curve a) is much easier than the one observed for *triethylborane* (see Fig. 1) since it occurs at a notably higher potential. This electroreduction of the trichloroester involves a non-reversible two-electron step whose peak potential is Ep$_c$ = -1.55 V. The cathodic peak

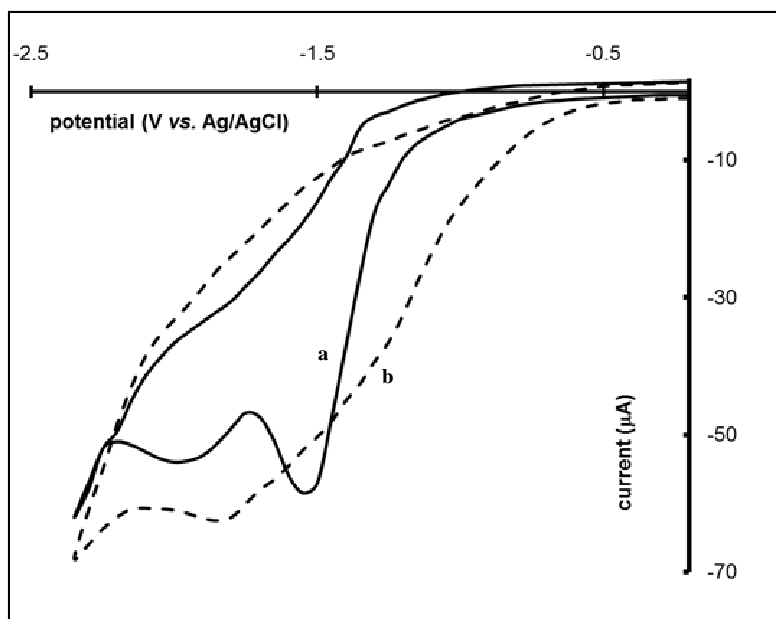**Fig. 2.** Cyclic voltammograms (0.1 V s$^{-1}$) in DMAc + Bu$_4$NBF$_4$ 0.2 mol dm$^{-3}$:
(a) trichloroester **1a** 4.5 10$^{-2}$ mol dm$^{-3}$ (b) + Et$_3$B 9.10$^{-2}$ mol dm$^{-3}$.

currents (i$_{pc}$) are a linear function of the square root of potential sweep rate, which is indicative of a diffusion-controlled process.

Addition of *triethylborane* (in excess) alters the voltammogram. The corresponding curve (Fig. 2, curve b) is not well shaped but shows that the bi-electronic and irreversible reduction of **1a** occurs at potentials slightly higher than those obtained in the absence of Et$_3$B. This can be explained by the Lewis acid property of *triethylborane*, which either coordinates with the carbonyl group, thus allowing an easier reduction of the chloroester **1a** (CE mechanism, Scheme 6-pathway 1), or reacts rapidly with the electrogenerated carbanion (EC mechanism, Scheme 6-pathway 2).

A second cathodic peak with a lower intensity is observed in the absence as well as in the presence of Et$_3$B, at about -2 and -1.85 V respectively. This signal can be imputed to the reduction of **1b** (see below) which arises from a partial protonation (*e.g.* by residual water) of the dichloroanion generated at the first reduction step. This also explains that byproducts **1b** and eventually **2b** were formed in appreciable amounts during electrolyses of solutions of **1a** + Et$_3$B (*cf.* ref. [1]).

The electroreduction of dichloroester **1b** is different from the one observed for **1a** since, in the absence of Et$_3$B, the voltammograms (Fig. 3, curve a) show two irreversible steps. Both current intensities correspond approximately to one electron per mole of **1b**. Referring to what has been reported for the electroreduction of chloroform [3, 4] this behavior results from the acidic properties of the starting material, as illustrated by Scheme 7.

The first step (Ep$_c$ = -1.3 V) is a two-electron reduction of **1b** generating the carbanion **12,** which yields **10** and **3** after protonation by **1b** itself. This proton exchange is favorable since the monochloroanion **12** is more basic than the dichloroanion **3**. The monochloroester **10**, then obtained, will be reduced at the second step (Ep$_c$ = -1.95 V).

When Et$_3$B is added, its electrophilic properties will induce the CE or EC mechanism presented in Scheme 6. Then, reaction with Et$_3$B competes with the reduction-protonation of **1b,** which allows recovery of a behavior similar to the one obtained from trichloroester **1a**.

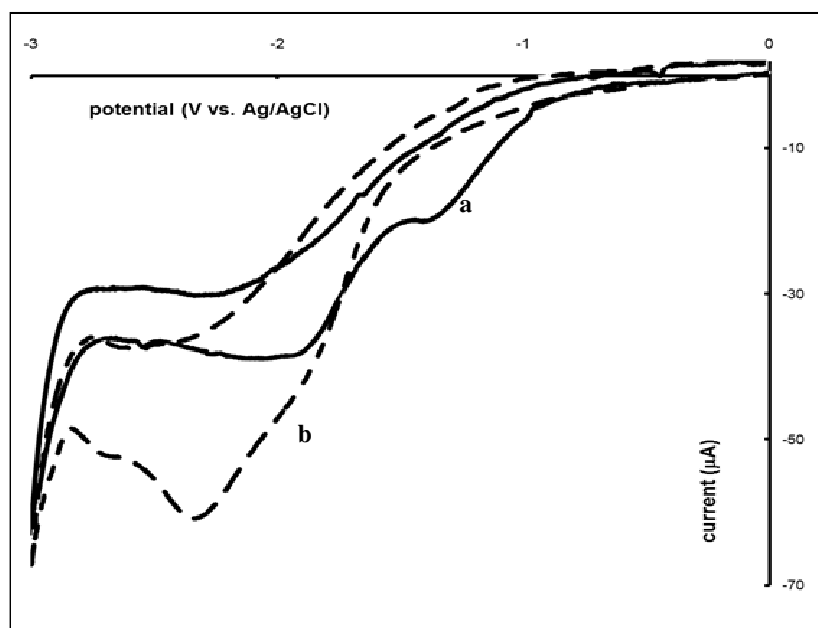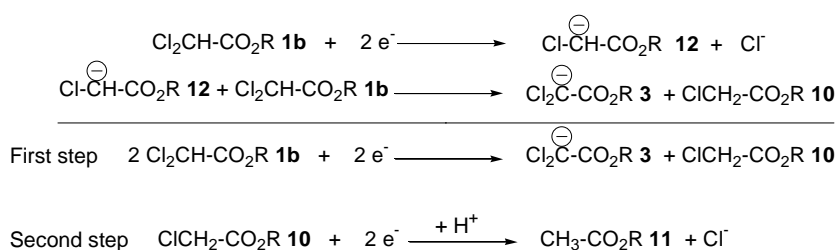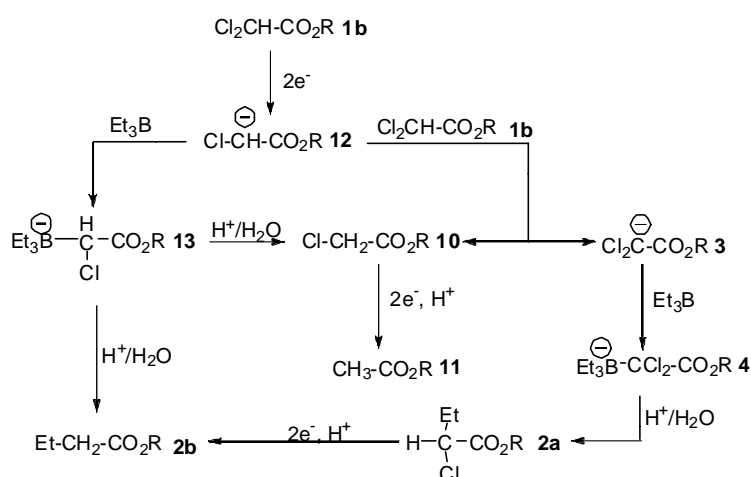The various reactions which can proceed from this competition are presented in Scheme 8.

**Scheme 6**



**Fig. 3.** Cyclic voltammograms (0.1 V s$^{-1}$) in DMAc + Bu$_4$NBF$_4$ 0.2 mol dm$^{-3}$: (a) dichloroester **1b** 4.5 10$^{-2}$ mol dm$^{-3}$ (b) + Et$_3$B 9.10$^{-2}$ mol dm$^{-3}$.



**Scheme 7**

This explains the results of the electrolytic reaction of **1b** with Et$_3$B where two alkylated compounds were simultaneously obtained (*cf.* Scheme 5). *Decyl butanoate* **2b** is the expected product resulting from the reaction between *triethylborane* and the electrogenerated carbanion **12**. *Decyl 2-chlorobutanoate* **2a** arises from the carbanion **3** generated by the acid-base reaction.
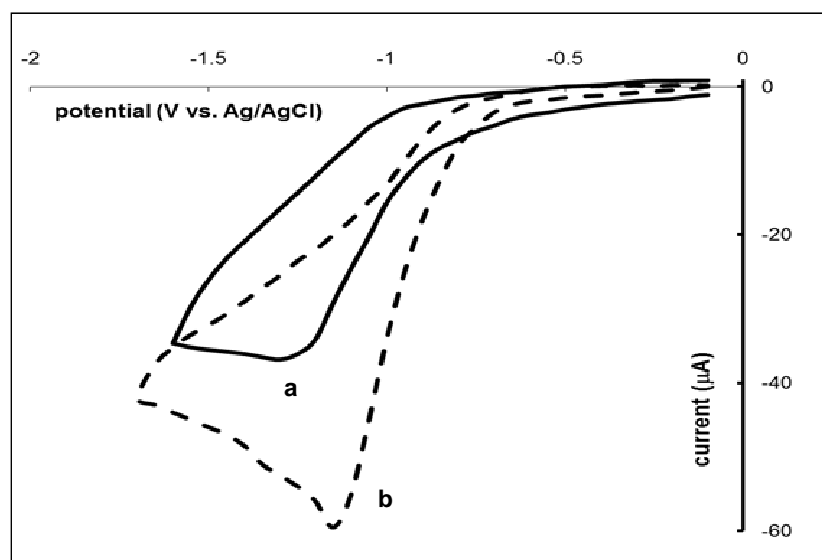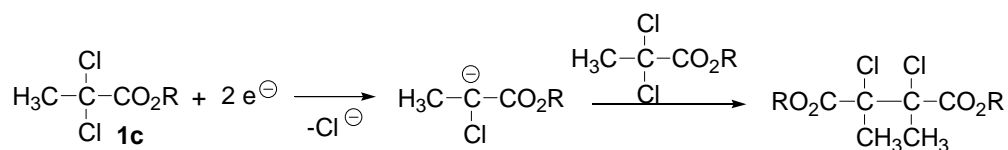
$Cl_2CH-CO_2R$ **1b**

$\downarrow$ $2e^-$

$Et_3B$ —— $Cl-\overset{\ominus}{C}H-CO_2R$ **12**  $\xrightarrow{Cl_2CH-CO_2R\ \textbf{1b}}$

$\downarrow$

$Et_3\overset{\ominus}{B}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-CO_2R$ **13** $\xrightarrow{H^+/H_2O}$ $Cl-CH_2-CO_2R$ **10** $\longleftarrow$ $Cl_2\overset{\ominus}{C}-CO_2R$ **3**

$\downarrow H^+/H_2O$ $\qquad\qquad\qquad\qquad$ $\downarrow 2e^-, H^+$ $\qquad\qquad$ $\downarrow Et_3B$

$\qquad\qquad\qquad\qquad\qquad CH_3-CO_2R$ **11** $\qquad$ $Et_3\overset{\ominus}{B}-CCl_2-CO_2R$ **4**

$Et-CH_2-CO_2R$ **2b** $\xleftarrow{2e^-,\ H^+}$ $H-\overset{\overset{Et}{|}}{\underset{\underset{Cl}{|}}{C}}-CO_2R$ **2a** $\xleftarrow{H^+/H_2O}$

**Scheme 8**



**Fig. 4.** Cyclic voltammograms (0.1 V s$^{-1}$) in DMAc + Bu$_4$NBF$_4$ 0.2 mol dm$^{-3}$: (a) dichloromethylester **1c** 4.5 10$^{-2}$ mol dm$^{-3}$ (b) + Et$_3$B 9.10$^{-2}$ mol dm$^{-3}$.

Compound **10** is obtained simultaneously but can also come in part (after hydrolysis) from the intermediate **13** if the chemical transfer reaction yielding **2a** from the chlorocarbanion ⁻ClCH-CO₂R and Et₃B is uncompleted.

As experimentally verified during electrosyntheses [1], a good method to convert **2a** into **2b** and at the same time to exclude **10** by its reduction into *decyl acetate* **11** consists in maintaining the electrolysis for an additional time after consumption of **1b**.

Thus, the yield in **2b** is notably increased (from 56 to 87%).

We have also examined the behavior of *dichloromethylester* Cl₂(CH₃)C-CO₂C₁₀H₂₁ **1c**, which has no acidic properties. Actually, this compound exhibits only one reduction step, but the corresponding voltammogram (Fig. 4, curve a) indicates that, in absence of Et₃B, the electroreduction of **1c** engages less than two electrons.

$$\underset{\textbf{1c}}{H_3C-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CO_2R} + 2\,e^\ominus \longrightarrow_{-Cl^\ominus} H_3C-\overset{\displaystyle \ominus}{\underset{\displaystyle Cl}{C}}-CO_2R \xrightarrow{H_3C-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CO_2R} \underset{CH_3 CH_3}{RO_2C-\overset{\displaystyle Cl}{C}-\overset{\displaystyle Cl}{C}-CO_2R}$$

**Scheme 9**

Indeed, it has already been reported that the chemical reduction (*e.g.* by divalent iron [5]) of alkyldichloroesters $RCl_2C\text{-}CO_2R'$ yields some dimer products like $R'O_2C\text{-}CCl(R)\text{-}CCl(R)\text{-}CO_2R'$. According to Scheme 9, we suppose that a similar reaction can be electrochemically induced by reaction between the electrogenerated carbanion $^-Cl(Me)C\text{-}CO_2C_{10}H_{21}$ and **1c**, which explains an apparent number of electrons lower than 2.

Addition of Et$_3$B allows finding a bielectronic electroreduction again (Fig. 4, curve b), as for compounds **1a** and **1b**. When Et$_3$B is added, coordination with **1c** either before or after its electroreduction (see Scheme 6) widely reduces the reductive dimerization and a quasi-bielectronic reduction is recovered.

From a synthetic point of view, when electrolyzing mixtures of **1c** and Et$_3$B, disappointing yield (47%) in alkylated product *decyl 2-methylbutanoate* **2c** was obtained [1]. Correlatively, several minor products (not isolated and not fully identified) which can result from a reductive homocoupling of **1c** (*e.g.* $R'O_2C\text{-}CX^1(Me)\text{-}CX^2(Me)\text{-}CO_2R'$ with $X^1$ and $X^2 = Cl$ or H) were evidenced by GC/MS. In order to limit this dimerization of **1c**, new electrosyntheses were carried out with a larger excess of Et$_3$B (2 equiv.). A significant improvement of the chemical yield was then obtained, since the corresponding alkylated product **2c** was recovered with 70% isolated yield.

**CONCLUSION**

From this study, it was evidenced that the electroreductive coupling of α-polychloroesters

with trialkylboranes proceeds via the bielectronic reduction of the chloroester. The electroreduction of trialkylborane is not involved since it occurs at much lower potentials.

The voltammograms corresponding to the reduction of the di- or tri-chloroesters are modified when Et$_3$B is added, indicating that a reaction occurs before or after the electrochemical step (CE or EC mechanism).

One side reaction is the protonation of the electrogenerated chlorocarbanion either by acidic impurities (*e.g.* residual water) or by the starting material itself in the case of $HCl_2C\text{-}CO_2R'$, which explains clearly the formation of the by-products obtained.

Another undesirable reaction which was observed particularly with the non acidic dichloromethylester $Cl_2(Me)C\text{-}CO_2R'$ is a reductive homocoupling of this compound. This competitive reaction is easily circumvented by adding an excess of trialkylborane.

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