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Mediated electrochemical reduction of dibromonorcarane in an emulsified system using Cr(II)

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High material yields were obtained in the indirect electrochemical reduction of 7,7-dibromobicyclo-[4-1-0]heptane (dibromonorcarane) to give the corresponding monobromo derivative in an ethylene chloride/water emulsion. The reducing agent was Cr(II) generated by current controlled electrolysis of aqueous chromic chloride at a silver cathode. The effect of the concentration of Cr(II) and the temperature was studied. At 0.1 M Cr(II) and at 40° C the best results were obtained (90% yield).

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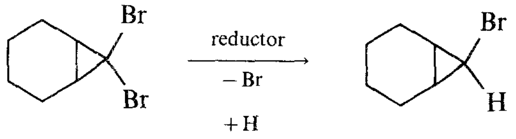
1. Introduction

The reduction of 7,7-dibromobicyclo[4-1-0]heptane (dibromonorcarane DBNC) to give 7-bromobicyclo-[4-1-0]heptane (monobromonorcarane MBNC)



has been carried out both chemically and electrochemically under a variety of experimental conditions. Reagents which serve for the former methods include strong reducing agents such as methyl-sulfinyl carbanion [1], Grignard reagent [2], sodium or lithium in alcohol [3], zinc dust [4] and different hydrides [5–7] among others. Temperatures around 80° C and quite long reaction times are necessary in order to achieve good yields.

Electrochemical reduction of DBNC has been performed on mercury at 0° C in various organic solvents. The electrolyses yielded 80–90% but rather negative potentials (~ 1.3 V vs SCE) had to be applied [8, 9].

The use of multiphase systems with a redox mediator offers a good alternative to both chemical and electrochemical methods for carrying out otherwise difficult reductions [10–12]. Products are formed by chemical reaction between a redox mediator and the organic substrate in an emulsion, coupled to the electrogeneration of the reducing agent on a suitable cathode [13–20].

Chromium (II) ion is a reductor widely used in organic chemical reactions [21]. Nevertheless, stepwise reduction of DBNC with chromium (II) sulphate in DMF gave only 30% of MBNC after 5 h reaction at 80° C [22]. It will be shown that it is possible to improve substantially on these results if experimental conditions are appropriately changed.

In previous work [23] the electroreduction of Cr(III) was studied on different cathodic materials and the best conditions for electrogeneration of Cr(II) *in situ* were established. A silver cathode was chosen for two main reasons: its relatively high overpotential for hydrogen evolution reaction (HER) and the possibility of carrying out the reduction of Cr(III) ions at relatively low potentials provided they were complexed as $Cr(H_2O)_5Cl^{2+}$ [24]. An acid medium was necessary to avoid chromic polynuclear complexes which polymerize on the electrode surface, but very low pH decreased the current efficiency due to HER competition. pH = 2 was found to be a good choice for both opposing trends [23 and references therein].

In the present paper indirect electrochemical reduction of DBNC in water-ethylene chloride emulsion using Cr(II) electrogenerated *in situ* as a reductor is reported as a simple and high yield procedure for MBNC synthesis.

2. Experimental details

All electrolyses were carried out at constant current in a two compartment cell using an asbestos membrane as separator to prevent back bromination of MBNC by bromine produced by oxidation on the anode.

The catholyte was an emulsion of 50 cm^3 of an aqueous phase of 0.1 M $NaClO_4$ (Merck PA) + 10^{-2} M $HClO_4$ (Carlo Erba RPE) + different concentrations of $CrCl_3$ (Carlo Erba RPE) and 20 cm^3 of organic phase of 0.05 M DBNC + 0.05 M tetrabutylammonium perchlorate ($TBAClO_4$) in 1,2-dichloroethane (Merck spectroscopic grade). $TBAClO_4$ was prepared from TBABr (Fluka AG purum) and $NaClO_4$ in water, recrystallized from water and dried at 30° C under vacuum. DBNC was synthesized according to [25] from bromoform (Carlo Erba RPE) and cyclohexene (obtained in our laboratory [26]).

The anode compartment was filled with 30 cm^3 of aqueous $NaClO_4$ (0.1 M) + $HClO_4$(0.01 M).

The emulsion was previously formed ultrasonically and maintained during the electrolyses by magnetic stirring. The system was deoxygenated with a stream

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Table 1. Effect of temperature and time on $Cr(H_2O)_5Cl^{2+}$ concentration. Aqueous solution composition: 0.05 M $CrCl_3$ + 0.1 M $NaClO_4$ + 10^{-2} M $HClO_4$. Absorbances were read at 630 nm for green $Cr(H_2O)_5Cl^{2+}$ and at 575 nm for blue $Cr(H_2O)_6^{3+}$ at 25° C after the samples were thermostatized at constant temperatures for 3.58 h

	Complex concentration (mol dm^{-3})	
t (° C)	*green* $Cr(H_2O)_5Cl^{2+}$	*blue* $Cr(H_2O)_6^{3+}$
0	*0.05*	–
15	*0.05*	–
20	*0.026*	*0.026*
40	*0.006*	*0.043*

of nitrogen (99.99%) before and during the experiments in order to avoid oxidation of Cr(II) ions by oxygen.

The cathode was an Ag wire (Carlo Erba 99.9%) of 80 cm^2 geometric area and the anode was a Pt gauze of large area.

In order to minimize HER, current densities were selected for each Cr(III) concentration by chronopotentiometry. The highest currents, for which the potential remained constant at −0.55 V vs SCE, were chosen. If currents higher than these values are applied, a transition time and a shift towards more negative potentials are observed with the corresponding improvement of HER.

The constant current source was a galvanostat from LyP Electrónica Argentina. Cyclic voltammetry was performed in the aqueous phase before and after the electrolyses, using equipment described elsewhere [23]. Temperatures were varied from 0° C to 40° C and controlled using a Lauda KR4 thermostat.

Two electrons per molecule for DBNC reductions were assumed, so electrolysis times are adjusted in order to give 2 F mol^{-1} of DBNC (193C). After the stoichiometric charge (calculated assuming a 100% DBNC conversion with 100% current efficiency) was passed, electrolyses were interrupted and the phases were allowed to separate. The organic phase was analysed by glc in a column packed with a 3% SE30 on Chromosorb G. A temperature programme between 50° C and 190° C at 10° C min^{-1} was found to give the best separation. Substrate and product were identified by comparison of retention times with those of standard solutions of authentic samples. Concentrations were estimated using chloronaphthalene as the internal standard.

The concentration of $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_6^{3+}$ complexes were determined by spectrophotometry in a MetroLab spectrophotometer. More experimental details are given in Table 1.

3. Results and discussion

Several electrolyses were carried out in water-ethylene chloride emulsions. The effect of $TBAClO_4$, Cr(III) concentrations, temperature and electrolysis time were analysed. After electrolyses, no other chromatographic peaks, apart from those of both MBNC isomers and of residual DBNC, were observed. The area under the peaks accounted for 83–97% of the starting material, depending on experimental conditions.

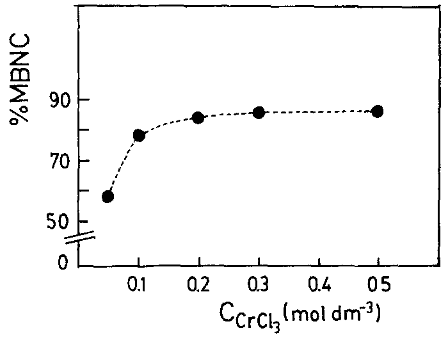


Fig. 1. Yields of MBNC as a function of Cr(III) concentration. Emulsion composition: 50 cm^3 of an aqueous phase of 0.1 M $NaClO_4$ + 10^{-2} M $HClO_4$ + $CrCl_3$ and 20 cm^3 of organic phase of 0.05 M DBNC + 0.05 M $TBAClO_4$ in 1,2-dichloroethane. Electrolyses were interrupted after 2 F mol^{-1} of DBNC. Currents were selected as explained in the text. T = 25° C. Percentages are referring to moles of starting material.

Although a small amount of MBNC could be produced in the absence of Cr(II) ions it is clear that yields were remarkably higher in the presence of the reducing agent. When the electrolyses are carried out in the absence of the redox mediator at $I = -40$ mA, for 1.34 h and $T = 0$° C, very low yields are obtained (10.2% of MBNC). If all the experimental conditions are kept constant but 0.1 M Cr(III) is added to the aqueous phase, the yield increases up to 61.7%.

Figure 1 shows the yield of MBNC for different Cr(III) concentrations at 25° C. The efficiency increased with starting Cr(III) concentration up to a percentage which could not be improved significantly by further increase in Cr(III) concentration.

When the electrolysis time was doubled at a constant current density, similar yields were obtained. Thus, two electrolyses performed at 0° C and at −40 mA for 1.5 h and 3.0 h gave 61.7% and 67.9% of MBNC, respectively.

Figure 2 shows the results obtained at different temperatures for two starting Cr(III) concentrations.

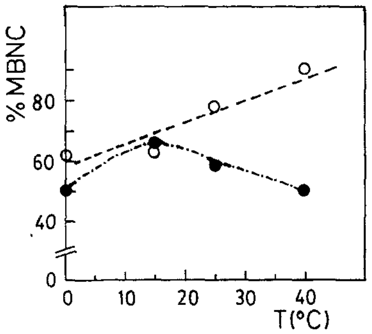
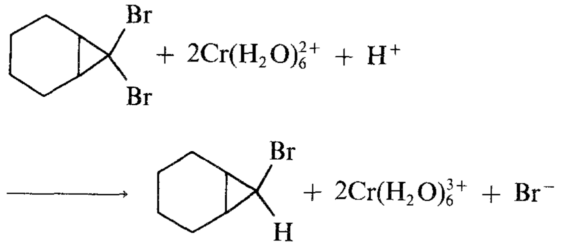


Fig. 2. Yields of MBNC as a function of temperature. Emulsion composition = 50 cm^3 aqueous 0.1 M $NaClO_4$ + 10^{-2} M $HClO_4$ + $CrCl_3$ + 20 cm^3 1,2-dichloroethane + 0.05 M DBNC + 0.05 M $TBAClO_4$. Electrolyses were interrupted after 2 F mol^{-1} of DBNC. (○) $CrCl_3$ concentration = 0.10 M, $I = -40$ mA, electrolysis time = 1.34 h. (●) $CrCl_3$ concentration = 0.05 M, $I = -15$ mA, electrolysis time = 3.58 h.

For 0.1 M Cr(III) solution it is clearly seen that steadily increasing yields were obtained as the temperature was raised, reaching virtually total conversion of DBNC at 40° C. Nevertheless, if the Cr(III) concentration is lower than 0.05 M, a maximum in DBNC reduction is observed around 15° C, then decreasing for higher temperatures. The chemical properties of Cr(III) complex ions have to be considered in order to understand the unexpected results. Cr(III) is readily reduced on silver at −0.55 V vs SCE (Reaction 1, Fig. 3) when the green complex $Cr(H_2O)_5Cl^{2+}$ is the electroactive species, but more negative potentials around −0.9 V are required for the reduction of the related $Cr(H_2O)_6^{3+}$ blue complex formed in aqueous solution either by a slow change in the coordination sphere composition [23 and references therein] (Reaction 2) or as a consequence of the reduction of the organic substrate (Reaction 3):

$$Cr(H_2O)_5Cl^{2+} + e^- \xrightleftharpoons{\text{silver cathode}} Cr(H_2O)_6^{2+} + Cl^- \tag{1}$$

$$Cr(H_2O)_5Cl^{2+} + H_2O \xrightarrow{\text{slow}} Cr(H_2O)_6^{3+} + Cl^- \tag{2}$$



(3)

In order to evaluate the amount of $Cr(H_2O)_6^{3+}$ formed in 0.05 M starting $Cr(H_2O)_5Cl^{2+}$ solution through Reaction 2, the optical density at 630 nm and 575 nm was determined before and after a lapse equivalent to the electrolysis time. Results are given in Table 1. No significant amount of $Cr(H_2O)_5Cl^{2+}$ was lost when the temperature was not higher than 15° C. On the contrary, almost all of the green complex was changed into the blue one at 40° C. The trend shown in Table 1 parallels that observed for MBNC yields in 0.05 M Cr(III) (Fig. 2).

In view of these facts, a two-fold effect of temperature on MBNC reduction may be recognized. First, temperature accelerates Reaction 2, lowering the electroactive green complex concentration. This effect should be more important at relatively low starting Cr(III) concentrations, thus explaining the decrease in yield observed in Fig. 2 for 0.05 M Cr(III). On the other hand, when the DBNC/Cr(III) ratio is lowered, temperature effects, namely the increase in chemical reduction rate and the more favourable partitional equilibrium conditions attained by organic substrate and reducing agent between both phases, should overcome the negative effect described above, accounting for the substantial increase in yield observed (Fig. 2).

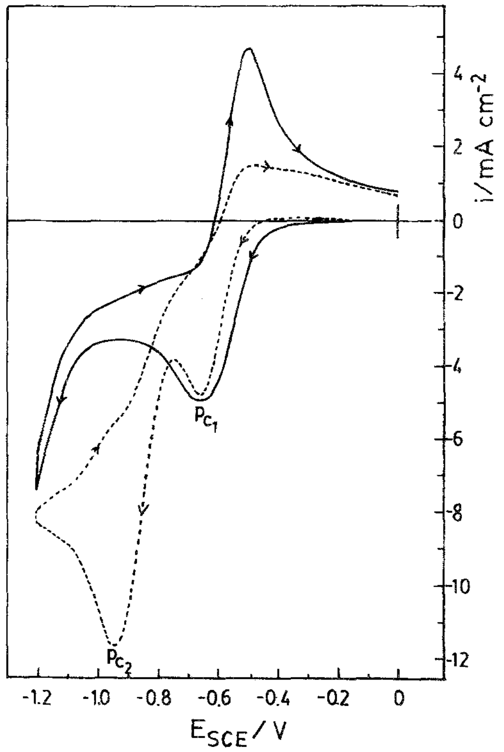


Fig. 3. Potentiodynamic *i*/*E* profiles of the aqueous phase 0.1 M $NaClO_4$ + 10^{-2} M $HClO_4$ + 0.05 M $CrCl_3$ on silver electrode before (——) and after (- - -) the electrolyses. Electrolysis time: 3.58 h, $I = -15$ mA, $T = 15°$ C, $v = 0.100$ V s^{-1}.

As a consequence of the electrolysis, the pH of the aqueous phase increased from 2 to 2.6, so buffering of the solution was not necessary.

Figure 3 shows the voltammetric *i*/*E* profiles of the aqueous phase on the silver electrode before and after an electrolysis. In the first case only one peak ($E_{1/2} = -0.55$ V vs SCE) attributable to the reduction of $Cr(H_2O)_5Cl^{2+}$ species is observed (p_{c_1}). After the electrolysis is carried out at a temperature low enough to minimize the loss of $Cr(H_2O)_5Cl^{2+}$ through Reaction 2 (15° C), a decrease in current for the p_{c_1} and a new peak (p_{c_2}) at more negative potentials are observed. This p_{c_2} can be assigned to the reduction of $Cr(H_2O)_6^{3+}$. The $E_{1/2}$ for this process is not clearly defined due to the HER overlapping. These experiments show that the organic substrate reduction does consume $Cr(H_2O)_6^{2+}$ and yields $Cr(H_2O)_6^{3+}$ (Reaction 3) differing from what occurs electrochemically through an internal sphere mechanism [23 and references therein] and in some homogeneous phase reactions [27]. Since $Cr(H_2O)_6^{3+}$ is not appreciably reduced at −0.55 V, under our experimental conditions, charge was used in the electrochemical generation of Cr(II) from starting $Cr(H_2O)_5Cl^{2+}$ ions but not for the cyclic regeneration of the reducing agent. Nevertheless, Cr(II) electrogenerated along with the chemical reduction process gives substantially better results. If complete electroreduction of Cr(III) is carried out prior to the addition of the organic phase to the cell, yields no higher than 30% were observed in good agreement with reports in the literature concerning DBNC reduction by chromium (II) sulphate [22].

Whether the reduction of DBNC proceeds via a radical or an anion intermediate is still controversial. Nevertheless, the second mechanism seems to be the more probable according to the literature [4, 9]. If this is the case, the H_2O dissolved in the organic phase should have an important role as proton donor. It is expected that $TBAClO_4$ will act as a phase transfer agent for hydrated anions (like Cl^-, coming from $CrCl_3$) increasing the extent to which water dissolves in 1,2 dichloroethane. A similar effect, but for dichloromethane, has been reported [19]. This assumption is confirmed by the results obtained when an electrolysis at 40° C and in 0.1 M $CrCl_3$ was carried out without $TBAClO_4$. Under these conditions the yield dropped from 91% to 59%.

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