



A Graphite Powder Cavity Cell as an Efficient Tool of Sustainable Chemistry: Electrocatalytic Homocoupling of 2-Halopyridines



Jadson L. Oliveira^a, Erwan Le Gall^b, Stéphane Sengmany^b, Eric Léonel^b, Pierre Dubot^c, Pierre Cénédèse^c, Marcelo Navarro^{a,*},¹

^a Departamento de Química Fundamental, CCEN, Universidade Federal de Pernambuco, av. Prof. Luis Freire S/N, 50740-901 Recife, Brazil

^b Electrochimie et Synthèse Organique, Institut de Chimie et des Matériaux Paris-Est UMR 7182CNRS, Université Paris-Est Créteil. 2-8 rue Henri Dunant, 94320 Thiais, France

^c Métaux et Céramiques à Microstructures Contrôlées, Institut de Chimie et des Matériaux Paris-Est UMR 7182CNRS, Université Paris-Est Créteil. 2-8 rue Henri Dunant, 94320 Thiais, France

ARTICLE INFO

Article history:

Received 12 March 2015

Received in revised form 13 May 2015

Accepted 14 May 2015

Available online 19 May 2015

Keywords:

electrosynthesis

cavity cell

graphite powder/carbon nanotubes

electrode

2,2'-bipyridine

nickel catalyst

ABSTRACT

A new electrochemical synthetic method for the transition metal-catalyzed homocoupling of 2-halopyridinic compounds into symmetrical 2,2'-bipyridines is described. Experiments were carried out in a cavity cell under various reaction conditions, using a nickel complex as catalyst, and controlled-potential or constant-current electrolyses. A graphite powder/carbon nanotube 9:1 ratio mixture proved to constitute the optimal cathode material. Excellent homocoupling product yields were observed using aqueous KCl solution as anolyte. The cathode material proved to be recyclable with possible reuse three times without notable loss of activity.

©2015 Elsevier Ltd. All rights reserved.

1. Introduction

In the last decades, electrochemistry has emerged as a relevant analytical tool to investigate mechanisms of organic reactions [1,2]. On the contrary, although electrosynthetic methodologies have been discovered more than one century ago [3], they have been globally underexploited, going through some periods of optimism that led, however, to their application in some industrial processes [4]. Recently, encouraged by the general interest of the organic community to the development of sustainable synthetic methodologies, the use of electrosynthesis has been magnified again, due to interesting features like the possible reduction or even minimization of polluting reagents, therefore addressing some green chemistry principles [5].

As the direct exchange of electrons between the electrode and organic reagents occurs through the addition of electron to the LUMO, or its withdrawal from the HOMO, according to the energies of the molecular orbitals [6,7], the selectivity of the reduction (or oxidation) reaction relies, in most cases, on energetic features of

molecular orbitals, especially according to the nature of substituent groups present on the molecules [8,9]. The direct electron transfer can lead to the formation of unstable intermediates that can rapidly react with many species present in the reaction medium, including the solvent itself [8]. In an effort to overcome practical problems (electrode material, divided cell, ohmic resistance, solvent/electrolyte, mass transfer, etc) encountered in electrosynthesis [9], we have recently developed a new electrochemical system involving a graphite powder-filled cell cavity, which acts as electrode during the electron exchange at the same time that operating as reaction medium [10]. Reagents introduced in the graphite powder cavity, before or after compaction, can be reduced (or oxidized) depending on the electrochemical potential or current applied. In some cases this cell enables the complete removal of the solvent as reaction medium [11–14], in other cases it is possible to reduce significantly its amount [10]. The auxiliary compartment can be composed of water and an ordinary electrolyte (KCl for example), taking into account the graphite hydrophobicity, thus maximizing the green side of the method [11].

Transition metals can be used to activate organic substrates associated to an electrochemical process [15]. Several nickel-electrocatalyzed reactions have been described: carboxylation of

* Corresponding author. Tel.: +55 81 21267460; fax: +55 81 21268442.

E-mail address: navarro@ufpe.br (M. Navarro).

¹ ISE member.

aryl halides [16], carboxylation of α -methylbenzyl halides [17], homocoupling of aryl halides [18], polymerization of organic dihalides [19] and heterocoupling of organic halides [20].

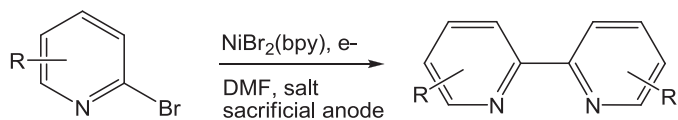
In the past years, we have undertaken efforts in the development of electrocatalytic methods for the homo or heterocoupling of haloaromatic and haloheteroaromatic compounds [21–27]. Such methods are very simple and efficient, giving notably very good yields of the respective dimers formed by the homocoupling reaction. Conditions are as follows: a nickel complex ($\text{NiBr}_2(\text{bpy})$) is used as catalyst, an undivided cell is employed, DMF is used as solvent and a sacrificial anode of Zn or Fe is employed (Scheme 1). The mechanism may proceed by two paths [28,15]. The first one, involving a reduction step of the nickel complex catalyst to Ni^0 , followed by an oxidative addition to the haloaromatic reagent. The $\text{arylNi}^{\text{II}}\text{X}$ adduct is reduced to arylNi^{I} , followed by a second oxidative addition ($\text{arylNi}^{\text{II}}\text{aryl}$) and the catalytic cycle is finalized by the reductive elimination of the homo or heterocoupling product [29,30]. As the paramagnetic intermediate arylNi^{I} has not been proved, a second competitive mechanism was proposed, in which $\text{arylNi}^{\text{II}}\text{X}$ undergoes a ligand scrambling, which gives $\text{arylNi}^{\text{II}}\text{aryl}$ and $\text{Ni}^{\text{II}}\text{X}_2$ [28]. The reductive elimination from $\text{arylNi}^{\text{II}}\text{aryl}$ gives the coupling product and Ni^0 complex, whereas $\text{Ni}^{\text{II}}\text{X}_2$ is recycled to Ni^0 by reduction on the cathode. The preparation of functionalized aryl- and heteroarylpyridazines has also been studied using this electrocatalytic method, in view of their potential pharmaceutical application [31,32].

2,2'-bipyridyl compounds are important chelating precursors used in obtaining metal complexes having the most diverse properties: luminescent, catalytic, electrochemical, electrical conductive, storage of solar energy, chiral molecular recognition and other more [28]. Therefore, because of the bipyridine importance and the necessity of development of cleaner synthetic ways, in this work we evaluate the reaction parameters for the application of the graphite powder cavity cell in the nickel-electrocatalyzed homocoupling of 2-bromopyridines, 2,6-dibromopyridine and 2,6-dichloropyridine. Application of such a technique in the preparative synthesis of 2,2'-bipyridines would bring several advantages over classical methods like minimizing the use of organic solvents, of the supporting electrolyte, and eliminating the requisite use of a sacrificial anode.

2. Experimental

2.1. Chemicals and general measurements

All chemicals were of reagent grade and were used without further purification. Distilled water was employed in all experiments. Graphite with two different particle size were purchased from Aldrich ($<20\ \mu\text{m}$) and Fluka ($<100\ \mu\text{m}$), multi-walled carbon nanotube was furnished by Federal University of Minas Gerais (5 to 60 nm diameter; 8 to 30 μm length). Graphite and CNT powders, nickel bromide and sodium iodide were dried over a Kugelrohr apparatus at 240 °C and at 120 °C, respectively, during 4 h under 5 mbars. Dimethylformamide was distilled over calcium hydride at 100 °C under 30 mbars.



R = H, CH_3 , Cl, Br

Scheme 1. Preparation of 2,2'-bipyridines using $\text{NiBr}_2(\text{bpy})$ as electrocatalyst.

Reactions were monitored by gas chromatography (GC) using a chromatograph fitted with a semi-volatile capillary column ($l=30\ \text{m}$, $\varnothing=0.25\ \text{mm}$, $df=0.25\ \mu\text{m}$) with a 40–250 °C temperature range ($10\ ^\circ\text{C}\ \text{min}^{-1}$) program. Calibration curves were carried out with different concentrations of reagents, by-products and dodecane (internal standard) for the quantification of substances after the reactions. NMR spectra were recorded in CDCl_3 at 400 MHz (^1H), 100 MHz (^{13}C). Melting points (mp) were measured on a capillary melting apparatus and are uncorrected. Chemical shifts (δ) are reported in parts per million (ppm) and calibrated according to the residual solvent signal. Coupling constant values (J) are given in hertz (Hz) and refer to apparent multiplicities, indicated as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets). Mass spectra (in electronic impact (EI^+) ionization mode) were measured on a GC-MS spectrometer.

2.2. General procedure of electrolysis

Linear sweep voltammetry, controlled-potential or constant-current electrolyses were carried out using Autolab PGSTAT 30 potentiostat/galvanostat and a home-made cavity cell (Fig. 1), described in the previous work [10]. The cathode compartment (a teflon cap assembly with a cylindrical cavity of 1.0 cm diameter vs. 0.5 cm depth) was prepared by addition of 300 mg of carbonaceous powder (pure graphite or mixed with multi-walled nanotubes). Then, the cathodic cavity was pressed, using an aluminum bar with the same diameter, with 2.5 kg weight (under $31.8\ \text{N}\ \text{cm}^{-2}$) during 10 min. In all experiments, 2-halopyridine, 2-halopicoline or 2,6-dihalopyridine reagents (0.5 mmol) and 30% NiBr_2 or 30% $\text{NiBr}_2(\text{bpy})$ were dissolved in 300 μL of $0.1\ \text{mol}\ \text{L}^{-1}$ NaI/DMF solution using a water bath ultrasound, then added dropwise into the pressed powder cathode. The cavity was then covered by a filter paper (used as separator membrane) and connected to the anodic compartment (a glass tube with a screw), filled with $0.1\ \text{mol}\ \text{L}^{-1}$ KCl solution. The cathode compartment bottom was connected to a graphite bar (1 cm diameter), and another graphite bar (1 cm diameter) was used as the anode. An Ag/AgCl, KCl (sat.) reference electrode was only employed in controlled-potential experiments. Constant-current electrolyses were carried out at -10 mA (6 hours) and -30 mA (4 hours). The theoretical charge calculated for 2-bromopyridine (0.5 mmol, 1 electron) reductions was $Q_t=48.24\ \text{C}$, and for nickel catalyst reduction (0.15 mmol, 2 electrons) $Q_t=28.95\ \text{C}$, furnishing a total theoretical charge $Q_t=77.19\ \text{C}$ for each electrolysis realized.

The scale-up electrolyses (5.0 mmol reagent) were carried out in a bigger cavity cell (2.0 cm cavity diameter vs. 0.9 cm depth), using 1.5 g of graphite/NTC (9:1), 1.0 mL of NaI/DMF solution and 25.0 mL of KCl aqueous solution $0.1\ \text{mol}\ \text{L}^{-1}$. Once the reaction was completed, (a) in one hand, the anodic compartment KCl solution was poured into 10 mL of a saturated EDTA solution, and the mixture extracted with $3 \times 10\ \text{mL}$ of CH_2Cl_2 . The combined anodic organic phases were dried over Na_2SO_4 ; (b) in another hand, the cathode material (graphite/CNT) was placed in a flask, the cavity rinsed with 10 mL CH_2Cl_2 and transferred to the same flask. Then, the system was closed and vigorously shaken. After the graphite/CNT solid decantation, the liquid was transferred by means of a Pasteur pipette to an Erlenmeyer and filtered. For GC quantification of by-products (pyridine or picoline) and reagents, 10 μL of dodecane (internal standard) were added to each 10 mL of organic phase (anodic or cathode). This cathode organic phase was then combined with the previous anodic organic phase, and evaporated under vacuum. The crude product was distilled on a Kugelrohr apparatus. DMF and other volatile by-products were first distilled between 50 °C and 120 °C, at 100 to 20 mbars, respectively, and the desired bipyridines derivatives between 120 °C and 230 °C, at 20 to 5 mbars, respectively.

Download English Version:

<https://daneshyari.com/en/article/183809>

Download Persian Version:

<https://daneshyari.com/article/183809>

[Daneshyari.com](https://daneshyari.com)