### Accepted Manuscript

Title: An activity scale of cathode materials for the electrochemical cyclisation of allyl 2-bromobenzyl ether

Authors: Bart Vanrenterghem, Tom Breugelmans



PII:	S0013-4686(17)30480-2
DOI:	http://dx.doi.org/doi:10.1016/j.electacta.2017.03.016
Reference:	EA 29050
To appear in:	Electrochimica Acta
Received date:	30-10-2016
Revised date:	3-3-2017
Accepted date:	3-3-2017

Please cite this article as: Bart Vanrenterghem, Tom Breugelmans, An activity scale of cathode materials for the electrochemical cyclisation of allyl 2-bromobenzyl ether, Electrochimica Acta http://dx.doi.org/10.1016/j.electacta.2017.03.016

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# An activity scale of cathode materials for the electrochemical cyclisation of allyl 2-bromobenzyl ether

Bart Vanrenterghem<sup>a\*</sup> and Tom Breugelmans<sup>a</sup>

<sup>a</sup> University of Antwerp, Research Group Advanced Reactor Technology, Universiteitsplein 1, 2610 Wilrijk, Belgium Corresponding author: <u>bart.vanrenterghem@uantwerpen.be</u>

#### Abstract

The electrocatalytic activity of 10 cathode materials (Ag, Au, Cu, Glassy carbon (GC), Ni, Mg, Mn, Pb, Pt and Ti) was examined for the intramolecular cyclisation reaction of allyl 2-bromobenzyl ether to 2-methyl benzopyran. The influence of the cathode materials on the electrocatalytic activity was tested by means of cyclic voltammetry (CV) in an electrolyte solution of allyl 2-bromobenzyl ether (1mM) + tetrabutylammonium perchlorate (0.1 M) (Bu<sub>4</sub>NClO<sub>4</sub>) in methanol (MeOH). On Au, GC, Ni, Mg, Mn, Pb and Pt one single reduction wave was measured while Ag and Cu exhibited two cathodic reduction waves. Ti did not show a voltammetric response. The best electrocatalytic activity was obtained on Ag which showed a shift of the reduction peak potential of 771 mV with respect to GC, the most inert material. In addition to the screening, rotating disk experiments (RDE) in combination with Koutecky Levich analysis and product formation during electrosynthesis were performed. Koutecky Levich analysis of the RDE at peak potential showed that one-electron transferred at Au, GC, Ni, Mg, Mn, Pb and Pt. On Ag and Cu the number of transferred electrons determined with Koutecky-Levich depends on the potential and can be tuned to specific one- or two-electron transfer. Electrosynthesis showed that on Au, GC, Ni, Mg, Mn, Pb and Pt exclusively 5-methyl benzopyran was formed. On Ag and Cu product formation was depended on the potential and 2-methyl benzopyran and allyl benzyl ether (not cyclized product) were both formed.

#### 1 Introduction

In recent years there is been a growing search for clean, catalytic and environmentally friendly methods for the synthesis of heterocyclic compounds [1]. The great interest for these molecules is due to important applications in pharmaceuticals [2]–[4], pesticides [5], dyes [6] and synthetic applications [7]. The classical organic synthesis of heterocycles is of a complex nature, requiring a large number of reaction steps and the use of auxiliaries which results in a low selectivity [1]. In addition the reaction is often catalysed by tributyl tinhydride (Bu<sub>3</sub>SnH) [8]–[10]. The high neurotoxicity and difficulties for a total removal of tin out of the reaction mixture have triggered the search for other alternative synthesis methods. Organic electrosynthesis may offer an interesting alternative i.e. the electron being a cheap, clean and energy efficient reagent [11].

Reductive radical cyclisation of aryl halides onto an unsaturated bond is frequently used to construct fused aromatics in heterocyclic organic synthesis [8], [12]. In Figure 1 the possible reaction mechanism that can occur is displayed. The reduction of aryl halides, certainly at inert electrodes, occurs through a dissociative electron transfer leading to the scission of the carbon-halogen bond [13], [14]. This process can occurs through 2 possible mechanisms. A first possibility, which is shown in equations 1 and 2 is that bond rupture occurs in a stepwise manner with the formation of an intermediate radical anion. The second possibility is the concerted way yielding directly in a radical anion (equation 3). After the radical is formed, it can undergo a cyclisation reaction after which it is reduced (equation 4 and 5) or it can be directly reduced, without cyclisation reaction (equation 6).

#### Figure 1: Possible reaction pathways to construct fused aromatic molecules starting from allyl 2-bromobenzyl ether

A disadvantage to the use of organic halides in electrosynthesis is that the electrochemical activation of C-X bonds, especially in chlorides and bromides, requires application of high negative potentials [15] . In addition, as shown in the previous equations (1-6), the reaction pathway is complex. The usage of an appropriate electrocatalyst to stimulate specific product formation is crucial to increase the selectivity. Several approaches based on homogeneous electrocatalysis, mainly with transition metals complexes [1], [8], [16]–[19], have been investigated to circumvent the high overpotential and selectivity. When the

carbon-halogen bond is reductively cleaved with electron-transfer mediators the potentials correspond to those of the reduction of the mediator. Although the formal electrode potential of the mediators is generally more positive than the potential required for direct reduction of carbon-halogen bond, this approach gives rise to low selectivity and difficulties for the purification of the reaction mixture. Attempts to overcome these obstacles for carbon-halogen bond activation are directed towards improving the catalytic activity of the electrode material by changing from homogeneous to heterogeneous catalysts [15].

Studies of the carbon-halogen bond rupture have already indicated the intrinsic potential of several bulk metals such as Ag, Ni or Cu [13], [15]. Jouikov et all. have for instance shown that functionalized graphene requires strongly negative potentials of ca. -1.8 V in non-aqueous media [20]. On the other hand Dunach et all. have shown that by using Ni complexes the high overpotential can be reduced [1], [18], [23]. Despite the large number of papers for homogeneous catalyst there is little work for the catalytic activity of heterogeneous bulk materials on the intermolecular cyclisation reaction. Hence there is a need for an electrochemical activity scale of cathode metals for the synthesis of heterocyclic compounds.

In this context, the aim of the present work will be to investigate the electrocatalytic activity of bulk metals as cathode material for the intramolecular cyclisation reaction. The electrocatalytic activity will be tested for the cyclisation reaction of allyl 2-bromobenzyl ether to 2-methyl benzopyran, which can be considered as a model reaction [8], [22]. The formation of benzopyran is of great importance for the pharmaceutical industry as it is an important building block for numerous drugs [23]. The purpose of this work is not to show the detailed reaction mechanism but to look at the overall reaction that occurs meaning the formation of allyl 2bromobenzyl ether or 2-methylbenzopyran.

Towards these directions our specific objectives are: (i) screening of Ag, Au, Cu, Glassy carbon (GC), Mg, Mn, Ni, Pb, Pt and Ti as cathode materials for the intramolecular cyclisation of allyl 2-bromobenzyl ether by means of cyclic voltammetry; (ii) study of the electron transfer through linear sweep voltammetry (LSV) in combination with rotating disk experiments (RDE) and (iii) batch electrosynthesis of 2-methyl benzopyran by means of experiments performed under potential control.

4

#### 2 Experimental

#### 2.1 Preparation of the cathode materials

10 cathode materials were selected for the screening; Ag, Au, Cu, Glassy carbon (GC), Mg, Mn, Ni, Pb, Pt and Ti. The choice of these materials is based on previous research regarding C-X bond rupture [15]. To exclude the influence of the morphology and consider only the intrinsic catalytic activity of the material all cathode materials where polished to prior extend. The polishing procedure consisted of a sequential polishing with 1 µm and 0.3 µm alumina powder (Struers). The electrochemical measurements were conducted with an autolab potentiostat/galvanostat PGSTAT 302F in a standard three-electrode electrochemical cell with a Pt wire counter electrode and Ag/AgCl (Saturated) reference electrode. The reference electrode was separated from the working electrode through a salt bride to prevent chloride or water contamination in the measurement medium.

The electrochemical characterisation of the different cathode materials was tested in a de-aerated electrolyte solution containing 0.1 M tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) (Acros, 99 %+) + 1 mM allyl 2-bromobenzyl ether (Sigma Aldrich, 95%) in MeOH (MeOH) (Sigma Aldrich, HPLC-grade). The rotation rate of the electrode was controlled with a radiometer CTV101.

Electrolysis experiments were carried out in a small volume (10 mL) electrochemical cell. The electrolyte was purged with nitrogen to remove all dissolved oxygen. Identical working-, reference- and counter electrodes were used as during the electrochemical characterisation. Experiments were carried out under potential control and identification and distribution were investigated with a Thermo Trace 1300 GC-FID in a stirred solution of 10 mM allyl 2—bromobenzyl ether. No additional preparation was done before injecting the sample on the column. Standards for product identification i.e. allyl benzyl ether (Enamine Store, 95%) and 2-methyl benzopyran (Enamine Store, 95%) were used without further purification steps.

#### 3 Results and discussion

#### 3.1. Screening of the cathode materials

At first the electrochemical behavior at less active cathode materials is investigate to benchmark the system. Recent research of the C-X bond rupture has indicated that materials such as GC, Pt and Ti can be candidates for an inert reference material, meaning that they are known to have slow kinetics of electron transfer to various redox systems and therefore require the highest overpotential for C-X bond activation [15], [24]. Before each experiment the ohmic drop was measured using EIS and compensated. The average ohmic drop for all experiments was ca. 80 ohms. Figure 2A and Table 1 show the results for the reduction of allyl 2bromobenzyl on GC. The current densities have been calculated in respect to the geometric surface area of the electrodes. A distinct cathodic wave can be observed with a peak potential of -1.92 V. When the reduction wave is measured at multiple scan rates between 50 mV s<sup>-1</sup> and 1 V s<sup>-1</sup> a good correlation (R<sup>2</sup>=0.9854, Table 1) is found between the peak current density and the square root of the scan rate. The reduction of allyl 2-bromobenzyl is thus characterized as a process of diffusive nature. When the concentration is elevated (Figure 2A) from 1 mM until 5 mM allyl 2-bromobenzyl ether, a linear correlation (0.9956, Table 1) is found with the peak current density while the reduction peak potential remained similar with maximum variations of 12mV (not shown).

# Figure 2: Cyclic voltammetry at 50 mV s-1 of GC (A-B), Ti (B) and Pt (B) in MeOH + $Bu_4NClO_4$ (0.1 M) and allyl 2-bromobenzyl ether 1mM (A-B) and 5mM (A)

# Table 1: Voltammetric data of GC, Pt and Ti for the reduction of allyl 2-bromobenzyl ether (1mM) + Bu<sub>4</sub>NClO<sub>4</sub> in MeOH measured at 50 mV s<sup>-1</sup>

In Figure 2B the CV features of Pt and Ti in comparison with GC are shown. On Pt the reduction peak is less pronounced and occurs at a potential of -1.71 V. Similar results in respect to GC are obtained when the relation between peak current density vs. square root of scan rate and concentration are investigated (Table 1).

With Ti no clear cathodic wave is measured even at higher concentrations. To verify that the low catalytic activity is caused by metallic Ti and not to the presence of a titanium (di)oxide layer, additional Surface Enhanced Raman Spectroscopy (SERS) measurements are done in this work. These measurements

(supporting information) confirm that no oxide layer is present whereby we believe that the low activity is due to purely metallic Ti. Since GC exhibits the clearest cathodic wave this will be used as reference material for all other materials.

Subsequently the electrochemical behavior on Ag, Au, Cu, Mg, Mn, Ni and Pb was studied. The investigated metals can roughly be divided in two groups: Figure 3A where a single reduction wave is measured (Au Pb, Mn, Mg and Ni) and Figure 3B where two closely spaced cathodic waves are observed (Ag, Cu).

The single reduction waves can be observed in Figure 3A between a potential window of -1.2 V and -2.5 V. The influence on the electrocatalytic activity is expressed as an electrocatalytic activity parameter in reference with GC, the material that requires the highest overpotential (Table 2);  $E_{p, cathode} -E_{p, GC}$ . This provides a scale for the electrocatalytic activity for each cathode material. Mn induces the greatest shift in reduction peak potential (260 mV) followed by Ni (150 mV) and Mg (140 mV). The influence of Au (112 mV) and especially Pb (39 mV) on the electrocatalytic activity is less pronounced. On all metals a good correlation is found between the peak current density and the square root of the scan rate and a good correlation is consistently found between the current density and concentration (Table 2).

#### Figure 3: Cyclic voltammetry at 50 mV s<sup>-1</sup> of Au (A), Ag (B) Cu (B), GC (A), Mg (A), Mn (A), Ni (A) and Pb (A) in MeOH + $Bu_4NCIO_4$ (0.1 M) and allyl 2-bromobenzyl ether 1mM

The CV features of Ag and Cu (Figure 3B) show an additional second reduction wave. The reduction peak potentials of Ag are respectively -1.15 V (Ag1, Table 2) and -1.38 V (Ag2, Table 2). At both potentials there is a linear correlation of the peak current density with square root of the scan rate and the process is of diffusive nature. At -1.15 V a linear correlation is found with the concentration while on -1.38 V the correlation is exponential between 1-5 mM allyl 2-bromobenzyl ether. The oxidation peak on Ag present at -0.68 V is believed to be due from the oxidation (1) of small amounts of H<sub>2</sub>0 present in the electrolyte and (2) dissolution of small quantities of Ag. Cu also shows two reduction peaks present at -1.68 V (Cu1) and -2.02 V (Cu2). The upper potential window of Cu is limited to prevent formation of CuO. At both potentials the process is characterized as diffusion control and a good correlation between the peak current density and concentration is measured (Table 2).

#### Table 2: Voltammetric data of Ag, Au, Cu, Mg, Mn, Ni and Pb for the reduction of allyl 2-bromobenzyl ether (1mM) + Bu<sub>4</sub>NClO<sub>4</sub> (0,1M) MeOH measured at 50 mV s<sup>-1</sup>

Regardless of the number of reduction peaks, both Cu and Ag show a good electrocatalytic with shifts of 239 mV and 771 mV respectively in comparison with GC (Table 2). It is the authors believe that the bond dissociation energy between Ag and Br reaches an optimal. The surface phenomena such as adsorption and desorption of intermediates and products play a crucial role in the electrocatalytic activity. The obtained results are in correspondence with previous findings for the electrosorption of halides on Ag and Cu and ion-metal interaction and their contribution to the beneficial catalytic activity [25]. The smaller current densities of Ag, compared to the other materials, is believed to be due to adsorption of Br<sup>-</sup> ions at potentials up to -1.2 V. Previous studies of Ocko et all. [26] have indicated that Br<sup>-</sup> coverage on Ag can reach up until 50% of the surface.

In addition to the CV measurements lineair sweep voltammetry was used in combination with rotating disk experiments (LSV/RDE) to elaborate the screening of cathode materials. The linear sweep voltammogram in this section is obtained at a scan rate of 1 mV s<sup>-1</sup> using a rotating disk electrode. In Figure 4 a rotating disk experiment is shown on a GC electrode. The potential is swept starting at -1.0 V and scanned in the negative direction until -2.2 V. The potential window is restricted until -2.2 V to prevent reduction of the solvent. When the system is scanned in an opposite direction from -2.2V until -1.0 V an identical voltammogram is obtained. The Koutecky Levich plot (Figure 4) is calculated at the reduction peak potential measured in previously obtained cyclic voltammogram (Figure 2 and Table 1). Calculations were done using equation 1 with values of  $D_R$ - 8.1x10<sup>-6</sup> cm<sup>2</sup>/s [27], v - 7.37x10<sup>-4</sup> cm<sup>2</sup>/s (kinematic viscosity) and C<sub>benzylbromide</sub>- 1mmol.

$$\frac{1}{j} = \frac{1}{Fk_f C_R^{Bulk}} + \frac{1}{0.62nFD_R^{2/3} v^{-1/6} C_R^{Bulk} \omega^{1/2}}$$
(1)

The calculated number of exchanged electrons on a GC cathode material is 1.05 (Table 3).

Figure 4: LSV recorded at 1mVs-1 with rotation rates of 3OO, 450, 620 and 743 RPM for the reduction of allyl 2-bromobenzyl ether (1mM) in MeOH +  $Bu_4NClO_4$  (0,1M).

On all other investigated cathode materials a single well-formed reduction wave is observed. The LSV curves can be consulted in the supporting information. To assess the influence of the cathode material on the reaction mechanism Koutecky-Levich analysis was applied to the reduction peak potentials measured in the previous section (Figure 3 and Table 2). Results of these calculations are shown in Table 3. The minimum correlation coefficient obtained in all these measurements is 0.9602. On Ag, Au, Cu, Mg, Mn, Ni ,Pb and Pt ca. one-electron is transferred. When Koutecky-Levich analysis is performed at the first reduction peak potential of Ag and Cu results show that, as with the other cathode materials, one-electron is transferred. However when Koutecky Levich analysis is applied to the second reduction peak potential 2 electrons are transferred.

# Table 3: Koutecky Levich analysis on investigated cathode materials performed at the reduction peak potential of allyl 2 bromobenzylether

#### 3.2. Product identification on different electrochemical materials

The mechanism of dissociative electron transfer of aryl halides is already previously reported and is known to proceed in a stepwise manner. Once more the authors like to stipulate that it is not our intention to give a detailed description of reaction mechanism but to clarify the overall processes which occur at different electrocatalytic materials. The product identification was done by GC-FID of experiments performed under potential control.

The experiments are performed under potential control i.e. the reduction peak potential (Table 1-2). The results of the experiments under potential control are divided in two groups: (1) where a single reduction peak is visible in the CV measurements (Figure 3A), shown in Figure 5 and (2) where two cathodic waves are observed (Figure 3B), shown in Figure 6.

In Figure 5A-B where the potential is set at the reduction peak potential, the yield of 2-methyl benzopyran on Au, GC, Mg, Mn, Ni, Pb and Pt is shown. For Ti the potential is set on -2.2 V since literature reports this as the potential where C-X bond activation takes place [15]. Analysis shows that only 2-methyl benzopyran is

formed on all of these cathode materials. The results are in correspondence with the previously performed Koutecky Levich analysis. The highest yield (Table 4) is obtained with Au (48 mol%), Mg (46 mol%), Ni (50 mol%) and Glassy carbon (44 mol%). Mn, Ti, Pb, Pt display a lower yield of respectively 35 mol%, 5 mol%, 32 mol% and 6 mol% (Table 4). This is as expected according to Faradays law, since the current densities recorded during the CV (Figure 2-3) are proportional with the yield. Next to the formed product, on all electrodes, also unreacted allyl 2-bromobenzyl ether was found.

# Figure 5: Product formation at E<sub>p</sub> on Au (B), GC (A), Mg (B), Mn (B), Ni (B), Pt (A), Pb (B) and Ti (A) in MeOH + Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) and allyl 2-bromobenzyl ether (10 mM)

#### Table 4: Yield of 2-methyl benzopyran formed at the reduction peak potential

At Ag and Cu product formation is studied at both the first and second reduction wave. On Ag at the first reduction wave only the formation of 2-methyl benzopyran occurs resulting in a yield of 48 mol% for Ag (Table 4-Figure 6, Ag1). At the second reduction peak potential (Ag2) 15 mol% 2-methyl benzopyran is formed (Table 4, Ag2). After 180 minutes an equilibrium is obtained for both curves with a maximum conversion. At the potentials of the second reduction wave, however, both the formation of 2- methyl benzopyran and allyl benzyl ether occurs. In fact, as already indicated with the Koutecky Levich analysis, a different number of electrons was transferred. Results indicate that the yield of allyl benzyl ether (52 mol%) exceeds that of 2-methyl benzopyran (15 mol%) (Table 4). By varying the potential with 243 mV the reaction can be controlled to specifically the formation of allyl 2-bromobenzyl ether of 2-methyl benzopyran on Ag. On Cu similar results are obtained. At the first reduction wave only the formation of 2-methyl benzopyran appears with a yield of respectively 56 mol% (Table 4, Cu1). The second reduction wave mainly gives rise to the formation of allyl 2-bromobenzylether with a yield of 73 mol% while conversion until 2-methyl benzopyran is decreased until 8 mol%.

Figure 6: Product formation of 2-methyl benzopyran at  $E_p$  of Ag1 and Cu1 in MeOH + Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) and allyl 2-bromobenzyl ether (10mM) until

#### 4 Conclusion

An electrochemical activity scale was built up for the intramolecular cyclisation reaction of allyl 2bromobenzyl ether to 2-methyl benzopyran in MeOH + 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>. CV measurements of GC, Pt, Au, Mg, Ni and Pb resulted in a single reduction wave. On Ag and Cu two distinct reduction peaks are measured. Ti did not exhibit a clear reduction peak. Out of all of the investigated cathode materials Ag exhibits the largest shift of 771mV in reference to GC followed by Mn (260 mV), Cu (238 mV), Ni (150mV), Mg (140), Au (112mV), and Pb (39mV). Koutecky Levich analysis at the peak potential of Au, GC, Mg, Mn, Ni, Pb, Pt and Ti showed that one-electron was transferred. On Ag and Cu at the first reduction peak potential similar results were obtained and results showed one-electron is transferred. However at the second, more negative reduction peak potential, the process shifted from one-electron transfer. In addition product formation was studied on the investigated materials. It was shown that on the reduction potential of GC, Pt, Au, Mg, Ni and Pb only 2-methyl benzopyran was formed. On Ag and Cu 2-methyl benzopyran was formed at the potential of first reduction peak while at the second reduction peak a mixture of 2-methyl benzopyran but mostly allyl-2 bromobenzyl ether was found. The highest yield for the electrosynthesis experiments of 2-methyl benzopyran were obtained at the first reduction peak of Ag (48 mol%) and Cu (56 mol%) and at the reduction peaks potential of Ni (50 mol%) Au (48 mol%) and Mg (46 mol%).

#### References

- [1] E. Duñach, M. José Medeiros, and S. Olivero, "Intramolecular reductive cyclisations using electrochemistry: development of environmentally friendly synthetic methodologies," *New J. Chem.*, vol. 30, no. 11, p. 1534, 2006.
- [2] L. Pieters, S. Van Dyck, M. Gao, R. Bai, E. Hamel, A Vlietinck, and G. Lemière, "Synthesis and biological evaluation of dihydrobenzofuran lignans and related compounds as potential antitumor agents that inhibit tubulin polymerization.," *J. Med. Chem.*, vol. 42, no. 26, pp. 5475–5481, 1999.
- [3] H. F. Roaiah, S. S. El-nakkady, W. S. El-serwy, M. A. A. Ali, and A. H. A. El-rahman, "Studies on some Benzopyran Derivatives with Expected Antimicrobial and Antiviral Activity," *Nature and Science*, vol. 8, no. 7, pp. 20–29, 2010.
- [4] M. M. Burbuliene, V. Jakubkiene, G. Mekuskiene, E. Udrenaite, R. Smicius, and P. Vainilavicius, "Synthesis and anti-inflammatory activity of derivatives of 5-[(2-disubstitutedamino-6-methylpyrimidin-4-yl)-sulfanylmethyl]-3H-1,3,4-oxadiazole-2-thiones," *Farmaco*, vol. 59, no. 10, pp. 767– 774, Oct. 2004.
- [5] E. Ayranci and N. Hoda, "Adsorption kinetics and isotherms of pesticides onto activated carboncloth.," *Chemosphere*, vol. 60, no. 11, pp. 1600–7, Sep. 2005.
- [6] A. S. Shawali, "Synthesis and tautomerism of aryl- and hetaryl-azo derivatives of bi- and triheterocycles," J. Adv. Res., vol. 1, no. 4, pp. 255–290, Oct. 2010.
- [7] K. C. Majumdar, P. K. Basu, and S. K. Chattopadhyay, "Formation of five- and six-membered heterocyclic rings under radical cyclisation conditions," *Tetrahedron*, vol. 63, no. 4, pp. 793–826, Jan. 2007.
- [8] E. Duñach, A. P. Esteves, M. J. Medeiros, C. S. dos Santos Neves, and S. Olivero, "Radical-type reactions in protic and aprotic media: Comparisons in nickel-catalysed electrochemical reductive cyclisations," *Comptes Rendus Chim.*, vol. 12, no. 8, pp. 889–894, Aug. 2009.
- [9] K. Mitsudo, Y. Nakagawa, J. Mizukawa, H. Tanaka, R. Akaba, T. Okada, and S. Suga, "Electro-reductive cyclization of aryl halides promoted by fluorene derivatives," *Electrochim. Acta*, vol. 82, pp. 444–449, Nov. 2012.
- [10] M. J. Medeiros, C. S. S. Neves, a. R. Pereira, and E. Duñach, "Electroreductive intramolecular cyclisation of bromoalkoxylated derivatives catalysed by nickel(I) tetramethylcyclam in 'green' media," *Electrochim. Acta*, vol. 56, no. 12, pp. 4498–4503, Apr. 2011.
- [11] H. J. Schäfer, "Contributions of organic electrosynthesis to green chemistry," *Comptes Rendus Chim.*, vol. 14, no. 7–8, pp. 745–765, Jul. 2011.
- [12] C.G. Sowell, R.L. Wollin and R.D. Little, "Electroreductive cyclization reaction, stereoselectino creation of quaternary centres in bicyclic frameworks and a formal total synthesis of quadrone," *Tetrahedron letters*, vol. 31, no. 4, pp. 95–98, 1990.
- [13] A. A. Isse, S. Gottardello, C. Durante, and A. Gennaro, "Dissociative electron transfer to organic chlorides: electrocatalysis at metal cathodes.," *Phys. Chem. Chem. Phys.*, vol. 10, no. 17, pp. 2409–16, May 2008.
- [14] A. A. Isse, G. Berzi, L. Falciola, M. Rossi, P. R. Mussini, and A. Gennaro, "Electrocatalysis and electron transfer mechanisms in the reduction of organic halides at Ag," J. Appl. Electrochem., vol. 39, no. 11, pp. 2217–2225, Jan. 2009.
- [15] C. Bellomunno, D. Bonanomi, L. Falciola, M. Longhi, P. R. Mussini, L. M. Doubova, and G. Di Silvestro,

"Building up an electrocatalytic activity scale of cathode materials for organic halide reductions," *Electrochim. Acta*, vol. 50, no. 11, pp. 2331–2341, Apr. 2005.

- [16] S. Olivero, J. Claude, and E. Dunach, "Electrochemical Intramolecular Reductive Cyclisation catalysed by electrogenerated Ni(cyclam)2+," *Tetrahedron Letters*, vol. 36, no. 25, pp. 4429–4432, 1995.
- [17] X. Chaminade, E. Duñach, A. P. Esteves, M. J. Medeiros, C. S. Neves, and S. Olivero, "Electrosynthesis of nitrogen heterocycles using environmentally friendly methodologies," *Electrochim. Acta*, vol. 54, no. 22, pp. 5120–5126, Sep. 2009.
- [18] E. Duñach, a. . Esteves, M. . Medeiros, D. Pletcher, and S. Olivero, "The study of nickel(II) and cobalt(II) complexes with a chiral salen derivative as catalysts for the electrochemical cyclisation of unsaturated 2-bromophenyl ethers," J. Electroanal. Chem., vol. 566, no. 1, pp. 39–45, May 2004.
- [19] A. Esteves, A. Freitas, M. Medeiros, and D. Pletcher, "Reductive intramolecular cyclisation of unsaturated halides by Ni(II) complexes," *J. Electroanal. Chem.*, vol. 499, no. 1, pp. 95–102, Feb. 2001.
- [20] V. Jouikov and J. Simonet, "Graphene: Large scale chemical functionalization by cathodic means," *Electrochem. commun.*, vol. 46, pp. 132–136, 2014.
- [21] E. Duñach, A. P. Esteves, L. F. M. Leite, M. A. Lemos, M. J. Medeiros, and S. Olivero, "Electrochemical Study of Nickel (salen) and Cobalt (salen) Derivatives Complexes in the Presence of Unsaturated Halides," *Portugaliae Electrochmica Acta*, vol 2, no. I, pp. 2–5.
- [22] E. Duñach, A. P. Esteves, A. M. Freitas, M. J. Medeiros, and S. Olivero, "Electroreductive cyclisation of unsaturated halides catalysed by nickel macrocyclic complexes," *Tetrahedron Lett.*, vol. 40, no. 49, pp. 8693–8696, Dec. 1999.
- [23] Rahman A.U. et all., "Current Pharamaceutical design," *Bentham Sci. Publ.*, vol. 1, no. 4, pp. 395–400, 2000.
- [24] A. Gennaro, A. A. Isse, E. Giussani, P. R. Mussini, I. Primerano, and M. Rossi, "Relationship between supporting electrolyte bulkiness and dissociative electron transfer at catalytic and non-catalytic electrodes," *Electrochim. Acta*, vol. 89, pp. 52–62, Feb. 2013.
- [25] G. Valette, "Ionic electrosorption on solid surfaces and congruence with respect to the electrical variable," *J. Electroanal. Chem. Interfacial Electrochem.*, vol. 146, no. 2, pp. 439–446, May 1983.
- [26] T. Wandlowski, J. X. Wang, and B. M. Ocko, "Adsorption of bromide at the Ag (100) electrode surface," *J. Electroan. Chem.*, vol. 500, pp. 418–434, 2001.
- [27] D. Zhou, H. Carrero, and J. F. Rusling, "Radical vs Anionic Pathway in Mediated Electrochemical Reduction of Benzyl Bromide in a Bicontinuous Microemulsion," *Langmuir*, vol. 3, no. c, pp. 3067– 3074, 1996.

Cathode	E <sub>p</sub> (V vs. Ag/AgCl)	J <sub>p</sub> (mA/cm²)	R² (J <sub>p</sub> vs v <sup>0,5</sup> )	R² (J <sub>p</sub> vs. C)
Glassy				
Carbon	-1.92	0.14	0.9854	0.9872
Pt	-1.71	0.02	0.9956	0.9793
Ті	/	/	/	/

Cathode	E <sub>p</sub> (V vs. Ag/AgCl)	J <sub>p</sub> (mA/cm²)	E <sub>p,cathode</sub> -E <sub>p, GC</sub> (mV)	R² (J <sub>p</sub> vs v <sup>0,5</sup> )	R² (J <sub>p</sub> vs. C)
Ag1	-1.15	0.08	771	0.9845	0.9699
Ag2	-1.38	0.02	/	/	0.9772
Au	-1.81	0.79	112	0.9955	0.9754
Cu1	-1.68	0.41	238	0.9779	0.9735
Cu2	-2.02	0.18	/	0.9821	0.9817
Mg	-1.78	0.07	140	0.9891	0.9821
Mn	-1.66	0.29	260	0.9903	0.9942
Ni	-1.77	0.14	150	0.9788	0.9837
Pb	-1.88	0.22	39	0.985	0.9844

		R² ( ω <sup>-1/2</sup> vs. J <sub>-</sub>
Cathode	n	1)
Ag1	1.07	0.9789
Ag2	2.18	0.9826
Au	1.12	0.9803
GC	1.05	0.9694
Cu1	1.09	0.9745
Cu2	2.05	0.9801
Mg	1.13	0.9924
Mn	0.97	0.9670
Ni	0.98	0.9716
Pb	1.20	0.9602
Pt	0.94	0.9627
Ті	/	/

Cathode	Yield allyl 2-bromobenzylether (mol%)	Yield 2-methyl benzopyran (mol%)	Yield allyl benzyl ether (mol%)
Ag1	52	48	0
Ag2	33	15	52
Au	52	48	0
GC	56	44	0
Cu1	44	56	0
Cu2	19	8	73
Mg	54	46	0
Mn	65	35	0
Ni	50	50	0
Pb	68	32	0
Pt	94	6	0
Ті	95	5	0

















