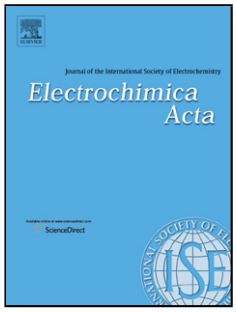

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Mediated electrolysis of vicinal diols by neocuproine palladium catalysts

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Abstract

Synthetic electrochemistry agrees well with the principles of sustainable chemistry, therefore it is considered as a more environmentally friendly approach than some current synthetic methods. Here, we present a new strategy for the chemoselective oxidation of vicinal diols, viz. the integration of neocuproine palladium catalysts and electrosynthesis. Benzoquinones are used as an effective mediator as the reduced species (hydroquinones) can be easily reoxidized at relative low potentials at an electrode surface. NeocuproinePd(OAc)$_2$ efficiently works as a catalyst in an electrolysis reaction for vicinal diols at room temperature. This is a remarkable observation given the fact that aerobic oxidation reactions of alcohols typically need a more complex catalyst, i.e. [neocuproinePdOAc]$_2$[OTf]$_2$. In this article we describe the optimization of the electrolysis conditions for the neocuproinePd(OAc)$_2$ catalyst to selectively oxidize diols. The suggested approach leads to conversion of alcohols with high yields and provides an interesting alternative to perform oxidation reactions under mild conditions by the aid of electrochemistry.

Keywords: palladium; benzoquinone; neocuproine ligand; alcohol oxidation; electrosynthesis

1. Introduction

Chemoselective oxidation reaction pathways aim to selectively oxidize an alcohol functionality in the presence of other alcohols. The oxidation of vicinal diols to the corresponding α-hydroxyketone functionality is of particular interest as this functionality is present in antitumor antibiotics such as kurasoin A and B [1] and in different natural products such as olivomycin A [2]. The α-hydroxyketone group also plays an important role in the modification of carbohydrates and other reaction schemes in general organic synthesis [3].

Different (non-electrochemical) methods have been proposed to achieve a chemoselective reaction of vicinal diols. The use of peroxotungstophosphates in combination with hydrogen peroxide is reported to give a selective oxidation of different vicinal diols [4]. Also, the stoichiometric use of dioxiranes results in chemoselectivity [5]. Another oxidation pathway consisting of $NaBrO_3$ with $NaHSO_3$ is described in literature to selectively oxidize cyclic vicinal diols to the corresponding hydroxyl ketones [6]. Focusing on catalytic systems using metal catalysts, the combination of $RuCl_3$ with buffered oxone as the stoichiometric oxidant is reported to oxidize different vicinal diols to the corresponding α-hydroxyketones [7]. Other catalysts are organotin compounds in combination with stoichiometric oxidants like Br_2 or N-iodosuccinimide (NIS) [8]. Those organotin catalysts can be also replaced by boronic acids [9], or used in combination with electrochemical oxidized bromo species (Br^+) [8,9].

In general, catalysts for alcohol oxidation can be immobilized on (modified) electrode surfaces, for example a carbon supported platinum electrode modified with bismuth. Using such an electrode glycerol is oxidized to dihydroxyacetone with high selectivity [10]. A second electrochemical approach includes TEMPO as a mediator and a similar selective

oxidation of glycerol to dihydroxyacetone can be obtained by reoxidizing TEMPO at the electrode surface. However, only a yield of 25 % is reported [11].

Palladium catalysts have been investigated thoroughly for the aerobic non-electrochemical oxidation of alcohols. Catalysts such as Pd carbene catalyst [12] or cationic pyridine based palladium complexes [13] have been reported for selective oxidation reactions with oxygen as stoichiometric oxidant. Another example of a palladium catalyst that can selectively oxidize vicinal diols is the cationic palladium complex using neocuproine as a ligand, developed by Waymouth et al [14].

The beneficial use of neocuproine as a ligand for palladium catalysts was first investigated by Sheldon et al. [15], they reasoned that the methyl groups on the 2 and 9 position of the phenanthroline ligand cause steric hindrance and thus prevent the formation of dimeric structures, resulting in a more active catalyst for oxidation reactions. The highest activity for the aerobic oxidation of alcohols was achieved by using the palladium catalyst neocuproinePd$(OAc)_2$ (Scheme 1, structure 1) which has a phenanthroline with two methyl groups substituents at the 2 and 9 position (neocuproine).

Scheme 1

Later, this catalyst was used as a basis for the synthesis of a new cationic palladium complex using neocuproine as a ligand [16]. It was reasoned that a cationic palladium complex with non-coordinating counter anions could increase the rate of aerobic alcohol oxidation. The dimeric acetate bridged [neocuproinePdOAc]$_2$[OTf]$_2$ (Scheme 1, structure 2) was synthesized by conproportionation of neocuproinePd$(OAc)_2$ and the ditriflate analogue neocuproinePd$(MeCN)_2(OTf)_2$. This catalyst 2 proved to have faster initial rates for the

aerobic oxidation of alcohols at room temperature. In comparison, catalyst 1 needs 80 degrees Celsius for an efficient conversion [15].

Interestingly, catalyst 2 allowed the selective oxidization of polyols [14]. More specific, in vicinal diols only the secondary alcohol is oxidized to the corresponding α-hydroxyketone. Also glycerol can be selectively oxidized to the corresponding dihydroxyacetone under mild conditions [17]. In those approaches both oxygen and p-benzoquinone are used as stoichiometric oxidants. Additionally, it was mentioned that catalyst 2 may convert unprotected pyranosyl glucosides to the corresponding ketosaccharides. Here, the catalyst can discriminate between different secondary hydroxyl groups, only the one at the C3 position is oxidized to the ketone by using 2,6-dichlorobenzoquinone as stoichiometric oxidants [18].

The drawback of using oxygen as the stoichiometric oxidant in combination with catalyst 2 is the fact that it may lead to the oxidation of the neocuproine ligand and corresponding losses in reactivity over time [16]. To avoid this, other catalysts have been synthesized. Waymouth et al. reported on a catalyst having a trifluoromethyl substituted phenanthroline ligand instead of neocuproine and studied its oxidation potential of 2-heptanol [19]. The results were not convincing, although the turnover number of this catalyst doubled and no ligand oxidation was observed, the initial rate, however, was 3.7 times lower compared to catalyst 2. Furthermore, the ligand is much more difficult to synthesize. Recently, a deuteration of the methyl substituents in the neocuproine ligand was suggested to obtain a more resistant ligand against oxidation [20].

In this article, an electrocatalytic approach by using catalyst 1 and 2 is suggested. By working in an inert gas atmosphere, the possible degradation of the catalyst by oxygen is prevented.

Secondly, the electrochemical recycling avoids the use of a stoichiometric amount (or excess) of the oxidants, making it a more sustainable alternative. In an electrocatalytic oxidation reaction, a mediator gets oxidized at the electrode surface at a low potential followed by the oxidation of the target molecule [21]. Mediators of interest are benzoquinones as it is known that the reduced species (hydroquinones) can be easily reoxidized at relative low potentials [22-26].

The selective oxidation of vicinal diols directly to α-hydroxy ketones is of utmost importance when looking for an atom-economical reaction. For the first time, palladium catalysts with neocuproine ligands are combined with the electrochemical recycling of benzoquinones. A selective electrochemical oxidation of diols under mild conditions and high yield is now presented.

2. Experimental

Synthesis of neocuproine$Pd(OAc)_2$ (catalyst 1)

A solution of neocuproine (5.5 mmol, 1.25 g) in anhydrous CH_2Cl_2 (20 mL) was added to a solution of $Pd(OAc)_2$ (5.0 mmol, 1.12 g) in anhydrous toluene (100 mL) at room temperature under nitrogen. The mixture was stirred overnight and heptane was added to precipitate the complex. A yellow solid was filtered off, washed with acetone and dried under vacuum; yield: 1.78 g (4.0 mmol, 80%).

Synthesis of neocuproine$Pd(CH_3CN)_2(OTf)_2$

To a slurry of catalyst 1 (0.221 g, 0.511 mmol) in acetonitrile (1.0 mL) was added a solution of triflic acid in acetonitrile (0.33 M, 3.8 mL, 2.5 equiv). The solution was stirred briefly and then precipitated with diethyl ether to give a yellow solid. This solid was isolated by

centrifugation, precipitated two more times from acetonitrile using diethyl ether, and dried under vacuum to give a light yellow solid (0.090 g). Additional triflic acid (0.33 M, 1.0 mL) was added to the original supernatant, followed by brief stirring and precipitation with diethyl ether. The resulting yellow solid was subjected to the same workup as described above to give additional product (0.021 g). The pure solids were combined (0.111 g, 0.160 mmol, 31% yield).

Synthesis of [neocuproinePdOAc]$_2$[OTf]$_2$ (catalyst 2)

To a 25 mL round-bottom flask with a stirbar was added catalyst 1 (0.0400 g, 0.0924 mmol), neocuproinePd(CH_3CN)$_2$(OTf)$_2$ (0.0642 g, 0.0924 mmol), and acetonitrile (10.0 mL). The resulting mixture was stirred until all solids dissolved and then precipitated with diethyl ether to give an orange solid. This solid was isolated by centrifugation, washed with diethyl ether, and dried under vacuum to give 1 as an orange solid (0.0589 g, 0.0563 mmol, 61% yield).

Electrochemical measurements

All electrochemical measurements were performed by using a Potentiostat/Galvanostat PGSTAT 30 from Metrohm Autolab, connected with a PC provided with NOVA 1.11 software. Cyclic voltammetry measurements were performed using a three electrode cell with a glassy carbon working electrode of 3 mm diameter (Metrohm, the Netherlands), a platinum sheet counter electrode and a bridged Ag/AgCl reference electrode with 2 M LiCl ethanol solution as inner solution and a 0.1 M Bu_4NBF_4 DMSO as bridge solution, all potentials mentioned are relative to this reference electrode which has a voltage difference of +150 mV versus a standard hydrogen electrode (SHE). The working electrode was pretreated by mechanical polishing. It was subjected to sequential polishing with a cloth covered with alumina powder

of 1 and 0.05 mm particle size (SPI supplies, USA) for 10 min. To remove any adherent Al_2O_3 particles, the electrode surface was rinsed thoroughly with deionized water and cleaned in an ultrasonic bath containing deionized water for 2 min. Next, the electrode was rinsed with acetone and dried. Solutions of 0.1 M Bu_4NBF_4 in DMSO were freshly made and purged with nitrogen gas for 10 minutes to remove oxygen before each measurement.

Electrolysis

A homemade airtight electrolysis cell was used equipped with a reticulated vitreous carbon (RVC) as working electrode (basi, USA), a bridged Ag/AgCl reference electrode with 2 M LiCl ethanol solution as inner solution and a 0.1 M Bu_4NBF_4 DMSO as bridge solution was used and the counter electrode, a platinum rod electrode, was put in a divided cell separated from the anodic part by a ceramic frit. In a typical electrolysis experiment 4 mL of a 0.2 M Bu_4NBF_4 DMSO solution was added to the divided part followed by the addition of 200 µL of acetic acid. In the anodic part neocuproine$Pd(OAc)_2$ (0.1 equivalent), 2,6-dimethoxybenzoquinone (0.6 equivalent) and the alcohol (0.7 mmol) was added to a 14 mL solution of 0.2 M Bu_4NBF_4 in DMSO. The cell was closed and put under an argon atmosphere. Stirring was started, next a potential of 0.7 V was applied. After the appropriate reaction time 30 mL of water was added to the reaction mixture. The resulting mixture was extracted with tert-butylmethylether (3 times 25 mL). The collected organic layer was washed with 15 mL of water to further remove DMSO. Next the organic layer was dried with $MgSO_4$ filtered and evaporated. The resulting solution was examined with NMR. Isolated products were obtained using column chromatography with heptane/ethylacetate (7/3) as eluent.

3. Results and discussion

A first set of experiments was performed to evaluate the reactivity of different palladium precursors for the selective oxidation of 1,2-octanediol, in combination with the electrochemical recycling of 2,6-dimethoxybenzoquinone. During the constant potential electrolysis (electrolysis cell equipped with a reticulated vitreous carbon (RVC) as working electrode) a current could be obtained and selective oxidation to the hydroxy ketone was observed (Table 1, entry 1).

The different palladium catalysts could convert the alcohol into the hydroxyl ketone during the electrolysis procedure. All three neocuproine ligated palladium catalysts gave a similar yield, as can be seen in Table 1. Only the palladium acetate (Table 1, entry 4) was not active, as almost no current was detected during the electrolysis. Next, both catalysts 1 and 2 were further tested in different solvents (DMSO, DMF and acetonitrile) (see Table S1). It was observed that DMSO is the solvent leading to the highest conversion. In DMF catalyst 1 seems to be not active while catalyst 2 is less active. In acetonitrile both catalysts seems to be inactive.

Surprisingly, neocuproinePd$(OAc)_2$ (catalyst 1) was also active in the electrolysis experiment at room temperature. Until now, only the aerobic oxidation of alcohols using this catalyst is reported at 80 degrees Celsius with the addition of a base. Only [neocuproinePdOAc]$_2$[OTf]$_2$ (catalyst 2) is reported to be active at room temperature with an excess of 2,6-dimethoxybenzoquinone. So, we expected an efficient electrochemical conversion at room temperature only for catalyst 2. Simultaneoulsy, we raised the question whether catalyst 1 is also reactive at room temperature with an excess of 2,6-dimethoxybenzoquinone (without

electrolysis). For this reason, different stoichiometric oxidations of 1,2-octanediol were performed with 2,6-dimethoxybenzoquinone and neocuproinePd$(OAc)_2$ at room temperature.

In literature, reoxidation of catalyst 2 is performed with p-benzoquinone instead of 2,6-dimethoxybenzoquinone as mediator. Therefore, a reaction was also tested with three equivalents of p-benzoquinone (Table 2, entry 3), no difference was observed between both mediators.

The oxidation reaction of 1,2-octanediol was further tested with three equivalents or 0.6 equivalents of 2,6-dimethoxybenzoquinone. In both cases only the stoichiometric oxidation of 1,2-octanediol was observed.

So, based on the comparison between electrolysis (Table 1) and stoichiometric oxidation (Table 2) of 1,2-octanediol, the electrochemistry clearly aids the facile conversion with high yield of the alcohol at room temperature in the presence of both catalyst 1 and catalyst 2.

To further examine the reactions responsible for the electrochemical oxidation of the alcohol, cyclic voltammetric experiments were performed. First, neocuproinePd$(OAc)_2$ was added to a DMSO electrolyte solution and scanned between the potentials of interest during the electrolysis. No redox peaks could be detected in a potential window from 0 to 1.0 V (Figure 1), at ca 1V a Pd feature occurs so this potential is further avoided to retain the activity of the catalyst. Next an excess of 1,2-octanediol is added to this solution and scanned in the same potential range with no observed redox processes. Finally 2,6-dimethoxybenzoquinone is added and here a redox peak could be detected around 0.6 V explained as the oxidation peak of 2,6-dimethoxyhydroquine. This reoxidation phenomenon explains the current monitored during the electrolysis experiment. A peculiar observation is the fact that the peak height is not in correlation with the concentration of the benzoquinone added elucidating a slow reoxidation process of the mediator.

Figure 1

With $[neocuproinePdOAc]_2[OTf]_2$ a similar experiment is conducted, resulting in a peak current which is ten times higher for the oxidation of 2,6-dimethoxyhydroquinone (Figure 2). A much more efficient reoxidation process of the mediator is thus taking place.

Figure 2

Experiments with a rotating disk electrode were performed. It can be seen that the limiting current (I_l) increases with the rotation rate (Figure 3). A linear relation between the limiting current and the square root of the rotation rate is detected which is according to the Levich equation (inset Figure 3).

Figure 3

Although the cyclic voltammetric experiments reveal differences of the two catalysts on a short time scale, a similar result (yield) is obtained during an electrolysis (ca seven hours) experiment under similar conditions. Probably, catalyst 1 has only a slower activation in the starting phase but at longer times a similar conversion is obtained. Faster initial rates with catalyst 2 were also observed in aerobic oxidation processes [16].

Since a similar yield is obtained during electrolysis, there is no advantage in using catalyst 2, being much more expensive and time-consuming synthesis. It was decided to further explore and optimize the electrolysis procedure using catalyst 1, the precursor of catalyst 2.

It has been shown in Table 1 that the electrolysis, combining neocuproinePd$(OAc)_2$ and 2,6-dimethoxybenzoquinone, results in the selective oxidation of 1,2-octanediol into the hydroxyl ketone. A conversion of ca 50% could be obtained. To optimize the reaction conditions during the electrolysis, different concentrations of 2,6-dimethoxybenzoquinone were added to examine the influence on the alcohol conversion.

From Table 3 it is clear that the addition of 2,6-dimethoxybenzoquinone is crucial to obtain an efficient oxidation reaction. The higher the concentration of benzoquinone, the more efficient the palladium catalyst can be reoxidized. As a result, the formed hydroquinone can be more efficiently oxidized at the electrode surface, proven by a higher charge obtained during the electrolysis. The optimized reaction conditions take place with 0.6 equivalents of 2,6-dimethoxybenzoquinone added, as a quasi-full conversion of the alcohol to the hydroxy ketone is detected (Table 3, entry 5).

Next, the influence of the concentration of the palladium catalyst on the conversion was examined. Lowering the concentration of the palladium catalyst results in a lower yield and hence in a lower charge; enough palladium catalyst should be present to obtain an efficient oxidation reaction. From Table 3 (entry 5-8) it is clear that 0.1 equivalents are needed to obtain an optimal conversion, ca. 85%.

Additionally, the influence of the nature of the mediator, benzoquinone, was investigated. An electrolysis reaction was performed using p-benzoquinone instead of 2,6-dimethoxybenzoquinone (Table 3, entry 3). As the oxidation potential of p-hydroquinone is shifted over +0.2 V compared to the one of 2,6-dimethoxyhydroquinone, a constant potential of 0.9 V instead of 0.7 V was applied. Comparable yields and efficiencies were found using these two quinones. Further optimization was conducted and also the influence of temperature was examined (Table 3, entry 9). A similar yield was obtained at 40 degrees Celsius as a reaction at room temperature so there is no benefit in using higher temperature.

The addition of a base was examined as it is known from literature that a high concentration of acetate is crucial to reoxidize the palladium catalyst in stoichiometric conversions using oxygen as stoichiometric oxidant. To our surprise, by adding 0.1 M of acetate (Table 3, entry 10) no electrolysis current could be detected and no oxidation of the 1,2-octanediol was observed. We noticed that the addition of acetate anions is making the palladium catalyst inactive. Also the addition of trimethylamine was tried (Table 3, entry 11) but again no current could be detected and only a small amount of the hydroxy ketone was formed.

The optimized procedure using 0.1 equivalents of catalyst 1 and 0.6 equivalents of 2,6-dimethoxybenzoquinone at room temperature under a constant potential of 0.7 V for 8 hours was expanded to different alcohols, firstly to elucidate the difference in conversion

between diols and singular alcohols. A primary and secondary aliphatic alcohol, 1-octanol (Table 4, entry 2) and 2-nonanol (Table 4, entry 3), were tested. Only an electrolysis current could be detected with 1-octanol, no current was detected with 2-nonanol. After work up, the aldehyde octanal was detected as a reaction product of the oxidation of 1-octanol and for the electrolysis of 2-nonanol the start product was mainly recovered. A test was also performed with 1-nonanol (Table 4, entry 4) and again oxidation of the alcohol took place with formation of the aldehyde nonanal in reasonable yield. So, the neocuproine catalyst seems capable to catalyze the oxidation of both vicinal diols (chemoselective) and also primary aliphatic alcohols.

Then, a primary and secondary benzylic alcohol were tested. A similar behavior was observed as with the oxidation of aliphatic alcohols. For benzyl alcohol (Table 4, entry 6), benzaldehyde was found as the oxidation product in a reasonable yield. In contrast, for 1-phenylethanol (Table 4, entry 5) no electrolysis could be detected, the starting alcohol was mostly recovered unaffected.

Comparing the results of the singular alcohols with 1,2-octanediol, the diol shows a better reactivity during the electrolysis (higher charge-yield). The presence of the two alcohol functions seems to be more easily activated by catalyst 1, an easier complexation is possible between the catalyst and the diol.

To further expand the scope of the suggested procedure, different diols were tested. Electrolysis of 1,2-hexanediol was performed (Table 5, entry 2) and a selective oxidation of the secondary alcohol was detected in a comparable yield as with 1,2-octanediol. Similar results were obtained with 1,2-decanediol (Table 5, entry 3).

By testing cyclohexanediol, the influence of two vicinal secondary alcohols instead of one primary and one secondary is studied. Using the standard electrolysis procedure also these alcohols were selectively oxidized to the hydroxy ketone. Similar yields of hydroxyl ketone were obtained starting from cis-cylcohexanediol and from trans-cyclohexanediol, illustrating that there is no preference for a certain configuration of the alcohol functionalities on the cyclohexane structure.

4. Conclusions

Neocuproine palladium based catalysts are of interest for the oxidation of vicinal diols in an electrolysis setup based on the electrochemical reoxidation of benzoquinone mediators.

The use of electrolysis in organic synthesis is an interesting pathway to obtain more green and sustainable synthesis procedures. Electricity and in essence electrons are used as a reagent and when combined with sustainable electricity generation this can lead to good alternatives for chemical oxidants.

The remarkable activity of the palladium catalyst neocuproine$Pd(OAc)_2$ in the electrolysis procedure provides an interesting alternative for the selective oxidation of vicinal alcohols at room temperature. Because of the reactivity of neocuproine$Pd(OAc)_2$ at room temperature, the cumbersome synthesis of more exotic Pd based catalysts is avoided while providing a similar reactivity using the same procedure.

The electrolysis procedure was evaluated and optimized by focusing on different singular and vicinal diols. For singular alcohols only the primary alcohols were oxidized. For the

vicinal diols, all tested compounds were active and a selective oxidation with good yield was obtained using the suggested electrolysis procedure.

References:

[1] R. Masuma, R. Uchida, K. Shiomi, T. Sunazuka, J. Inokoshi, T. Kawakubo, et al., Kurasoins A and B, New Protein Farnesyltransferase Inhibitors Produced by Paecilomyces sp. FO-3684. II. Structure Elucidation and Total Synthesis, J. Antibiot. 49 (1996) 886.

[2] V. Kumar, W.A. Remers, W.T. Bradner, Preparation and antitumor activity of olivomycin A analogs, J. Med. Chem. 23 (1980) 376–379.

[3] A. Minnaard, M. Witte, N. Eisink, Chemo- and Regioselective Oxidation of Secondary Alcohols in Vicinal Diols, Synthesis. 49 (2017) A–H.

[4] Y. Sakata, Y. Ishii, A versatile transformation of vic-diols into .alpha.-hydroxy ketones with hydrogen peroxide catalyzed by peroxotungstophosphates, J. Org. Chem. 56 (1991) 6233–6235.

[5] L. D'Accolti, A. Detomaso, C. Fusco, A. Rosa, R. Curci, Selective oxidation of optically active sec,sec-1,2-diols by dioxiranes. A practical method for the synthesis of homochiral .alpha.-hydroxy ketones in high optical purity, J. Org. Chem. 58 (1993) 3600–3601.

[6] M. Bierenstiel, P.J. D'Hondt, M. Schlaf, Investigations into the selective oxidation of vicinal diols to α-hydroxy ketones with the NaBrO3/NaHSO3 reagent: pH dependence, stoichiometry, substrates and origin of selectivity, Tetrahedron. 61 (2005) 4911–4917.

[7] B. Plietker, B. Plietker, The RuO 4 -Catalyzed Ketohydroxylation. Part 1. Development, Scope, and Limitation, J. Org. Chem. 69 (2004) 8287–8296.

[8] T. Maki, S. Iikawa, G. Mogami, H. Harasawa, Y. Matsumura, O. Onomura, Efficient Oxidation of 1,2-Diols into α-Hydroxyketones Catalyzed by Organotin Compounds, Chem. – Eur. J. 15 (2009) 5364–5370.

[9] M. Kuriyama, O. Onomura, Boronic Acid-Catalyzed Selective Oxidation of 1,2-Diols to α-Hydroxy Ketones in Water, Adv. Synth. Catal. 356 (2014) 934–940.

[10] Y. Kwon, Y. Birdja, I. Spanos, P. Rodriguez, M.T.M. Koper, Highly Selective Electro-Oxidation of Glycerol to Dihydroxyacetone on Platinum in the Presence of Bismuth, ACS Catal. 2 (2012) 759–764.

[11] R. Ciriminna, G. Palmisano, C. Della Pina, M. Rossi, M. Pagliaro, One-pot electrocatalytic oxidation of glycerol to DHA, Tetrahedron Lett. 47 (2006) 6993–6995.

[12] L. Bettucci, C. Bianchini, W. Oberhauser, T.-H. Hsiao, H.M. Lee, Chemoselective aerobic oxidation of unprotected diols catalyzed by Pd–(NHC) (NHC=N-heterocyclic carbene) complexes, J. Mol. Catal. A: Chem. 322 (2010) 63–72.

[13] L. Bettucci, C. Bianchini, J. Filippi, A. Lavacchi, W. Oberhauser, Chemoselective Aerobic Diol Oxidation by Palladium(II)–Pyridine Catalysis, Eur. J. Inorg. Chem. 2011 (2011) 1797–1805.

[14] K. Chung, S.M. Banik, A.G. de Crisci, D.M. Pearson, T.R. Blake, J.V. Olsson, et al., Chemoselective Pd-Catalyzed Oxidation of Polyols: Synthetic Scope and Mechanistic Studies, J. Am. Chem. Soc. 135 (2013) 7593–7602.

[15] G.-J. ten Brink, I.C. . Arends, M. Hoogenraad, G. Verspui, R. Sheldon, Catalytic Conversions in Water. Part 23: Steric Effects and Increased Substrate Scope in the Palladium-Neocuproine Catalyzed Aerobic Oxidation of Alcohols in Aqueous Solvents, Adv. Synth. Catal. 345 (2003) 1341–1352.

[16] N.R. Conley, L.A. Labios, D.M. Pearson, C.C.L. McCrory, R.M. Waymouth, Aerobic Alcohol Oxidation with Cationic Palladium Complexes: Insights into Catalyst Design and Decomposition, Organometallics. 26 (2007) 5447–5453.

[17] R.M. Painter, D.M. Pearson, R.M. Waymouth, Selective Catalytic Oxidation of Glycerol to Dihydroxyacetone, Angew. Chem., Int. Ed. 49 (2010) 9456–9459.

[18] M. Jäger, M. Hartmann, A.J. Minnaard, Catalytic Regioselective Oxidation of Glycosides, Angew. Chem., Int. Ed. 52 (2013) 7809–7812.

[19] D.M. Pearson, N.R. Conley, R.M. Waymouth, Oxidatively Resistant Ligands for Palladium-Catalyzed Aerobic Alcohol Oxidation, Organometallics. 30 (2011) 1445–1453.

[20] N. Armenise, N. Tahiri, N.N.H.M. Eisink, M. Denis, M. Jäger, J.G. de Vries, et al., Deuteration enhances catalyst lifetime in palladium-catalysed alcohol oxidation, Chem. Commun. 52 (2016) 2189–2191.

[21] R. Francke, R.D. Little, Redox catalysis in organic electrosynthesis: basic principles and recent developments, Chem. Soc. Rev. 43 (2014) 2492–2521.

[22] C. Amatore, C. Cammoun, A. Jutand, Pd(OAc)2/p-Benzoquinone-Catalyzed Anaerobic Electrooxidative Homocoupling of Arylboronic Acids, Arylboronates and Aryltrifluoroborates in DMF and/or Water, Eur. J. Org. Chem. 2008 (2008) 4567–4570.

[23] J. Lybaert, S. Trashin, B.U.W. Maes, K. De Wael, K.A. Tehrani, Cooperative Electrocatalytic and Chemoselective Alcohol Oxidation by Shvo's Catalyst, Adv. Synth. Catal. 359 (2017) 919-925.

[24] C. Amatore, C. Cammoun, A. Jutand, Electrochemical Recycling of Benzoquinone in the Pd/Benzoquinone-Catalyzed Heck-Type Reactions from Arenes, Adv. Synth. Catal. 349 (2007) 292–296.

[25] C. Amatore, C. Cammoun, A. Jutand, Palladium/Benzoquinone-Catalyzed Electrochemical Oxidation of Alcohols Under Anaerobic Conditions, Synlett. (2007) 2173–2178.

[26] P. Röse, S. Emge, C.A. König, G. Hilt, Efficient Oxidative Coupling of Arenes via Electrochemical Regeneration of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) under Mild Reaction Conditions, Adv. Synth. Catal. 359 (2017) 1359-1372.

Captions:

Figure 1. Cyclic voltammograms with a scan rate of 100 mVs^{-1} of an 0.1 M Bu_4NBF_4 DMSO solution at 20° C (blue); with addition of 0.9 mM neocuproinePd$(OAc)_2$ (black); with addition of 50 mM 1,2-octanediol (red); with addition of 8.9 mM 2,6-dimethoxybenzoquinone (green).

Figure 2. Cyclic voltammograms with a scan rate of 100 mVs^{-1} of an 0.1 M Bu_4NBF_4 DMSO solution at 20° C (blue); with addition of 0.9 mM [neocuproinePdOAc]$_2$[OTf]$_2$ (black); with addition of 50 mM 1,2-octanediol (red); with addition of 8.9 mM 2,6-dimethoxybenzoquinone (green).

Figure 3. Cyclic voltammograms with a scan rate of 100 mVs^{-1} of an 0.1 M Bu_4NBF_4 DMSO solution at 20° C with 0.9 mM [neocuproinePdOAc]$_2$[OTf]$_2$; 50 mM 1,2-octanediol (red); 8.9 mM 2,6-dimethoxybenzoquinone at different rotation rates: 500 (a); 1000 (b); 1500 (c); 2000 (d); 2500 (e) and 3000 (f) rpm. Inset: I_l versus $(\omega)^{1/2}$.

Scheme 1. Two neocuproine palladium catalysts: neocuproinePd$(OAc)_2$ (1) and [neocuproinePdOAc]$_2$[OTf]$_2$ (2).

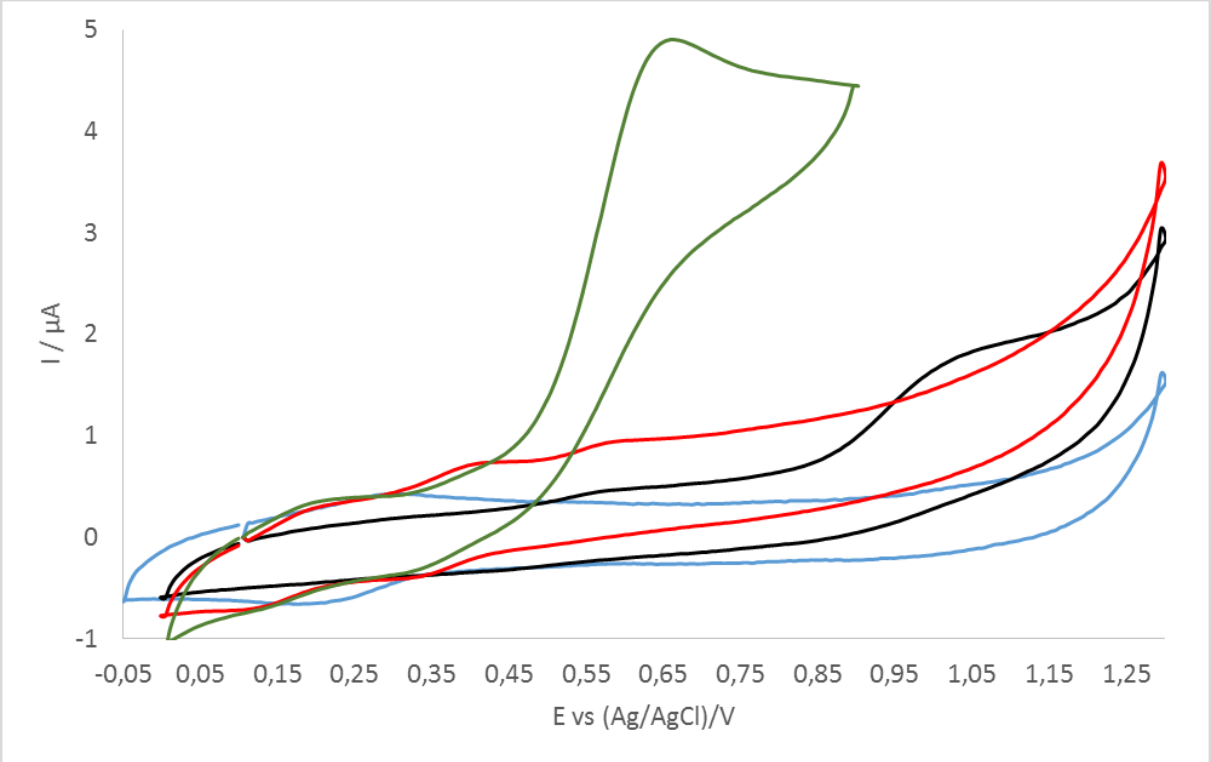


Figure 1

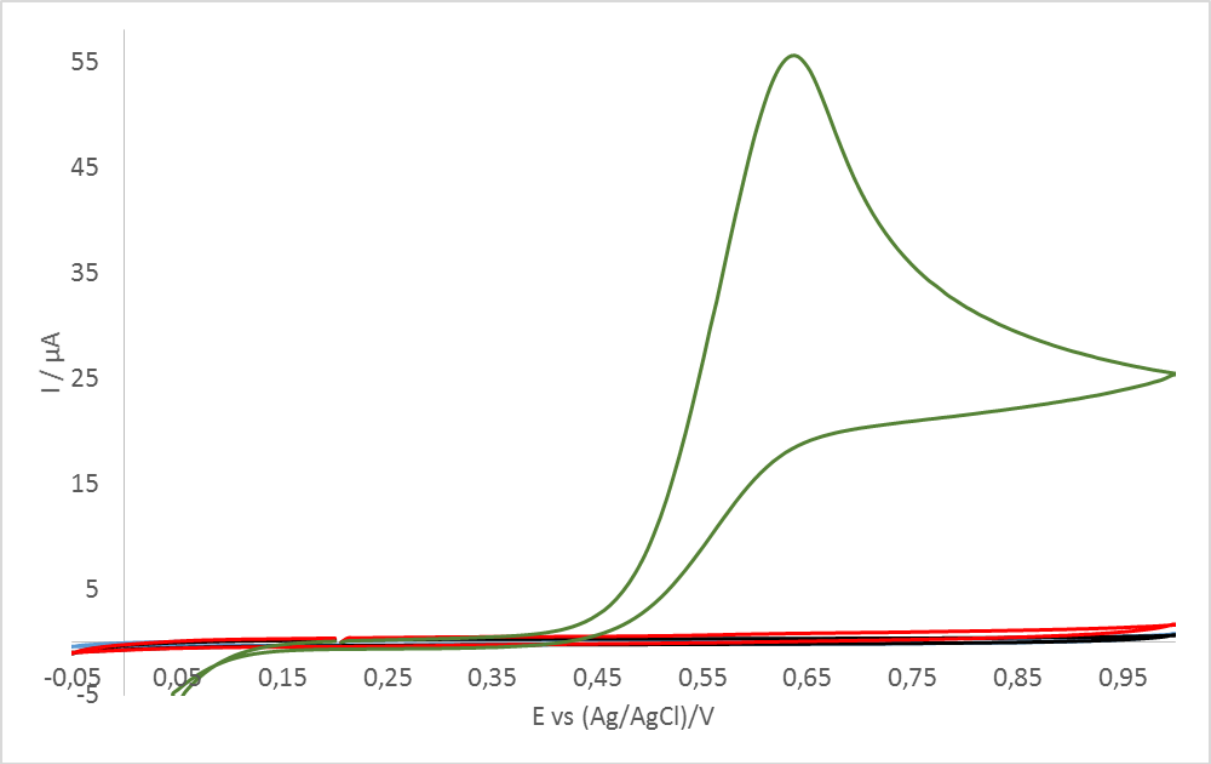


Figure 2

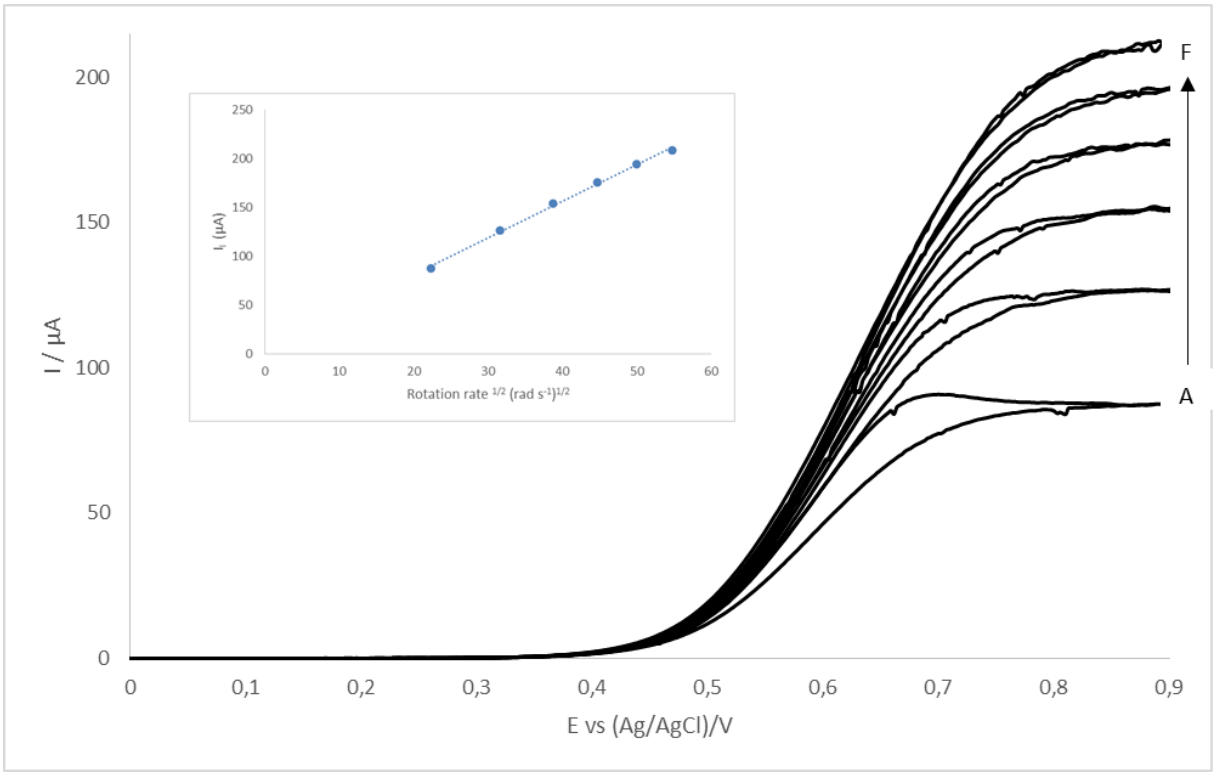
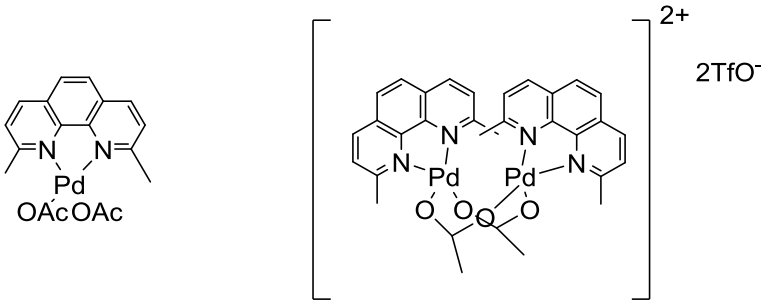


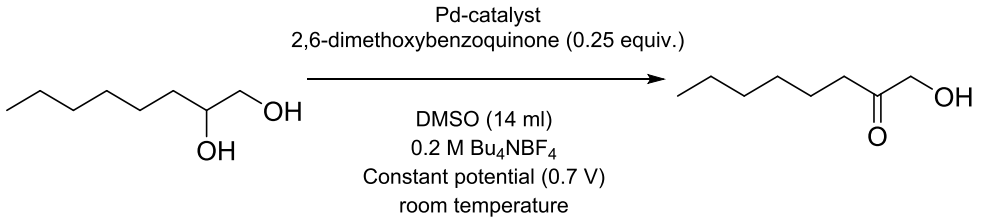
Figure 3



1 **2**

Scheme 1

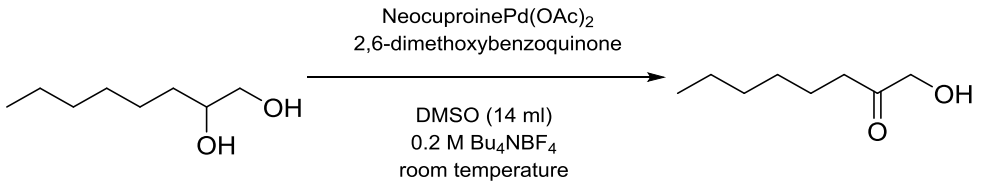
Table 1. Oxidation of 1,2-octanediol with different palladium catalysts with electrochemical recycling of 2,6-dimethoxybenzoquinone.



Entry[a)]	Palladium Catalyst	Time [h]	Yield [%][b]	Recovered alcohol [%][b]	Charge [Coulomb]
1	neocuproinePd(OAc)$_2$	7	49	34	70
2[c]	[neocuproinePdOAc]$_2$[OTf]$_2$	5	53	36	74
3	NeocuproinePd(CH$_3$CN)$_2$(OTf)$_2$	5	40	48	58
4	Pd(OAc)$_2$	5	5	90	4

[a)] reaction conditions: 0.7 mmol alcohol with 0.05 equivalents of palladium catalyst and 0.25 equivalents of 2,6-dimethoxybenzoquinone in 14 mL DMSO with 0.2 M Bu_4NBF_4 at room temperature with constant potential of 0.7 V under argon atmosphere.
[b)] NMR yields calculated after extraction with the addition of 1,3,5-trimethoxybenzene as an internal standard.
[c)] With 0.025 equivalents of (neocuproinePdOAc)$_2$(OTf)$_2$

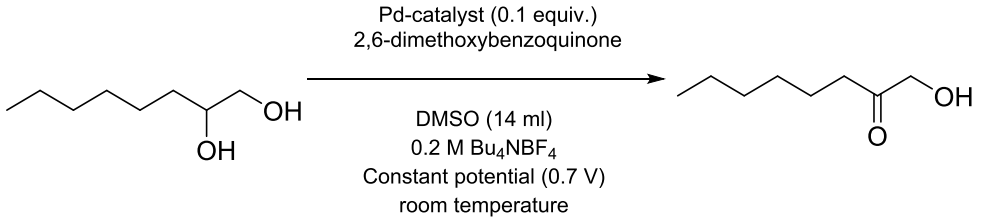
Table 2. Stoichiometric oxidation of 1,2-octanediol with 2,6-dimethoxybenzoquinone.



Entry[a]	Equivalent Benzoquinone	Time [h]	Potential	Yield [%][b]	Recovered alcohol [%][b]
1[c]	3 equiv.	6	No potential	4	95
2	3 equiv.	6	No potential	11	87
3[d]	3 equiv.	7	No potential	13	83
4	0.6 equiv.	8	No potential	9	87

[a)] reaction conditions: 0.7 mmol alcohol with 0.1 equivalents of neocuproinePd(OAc)$_2$ and x equivalents of 2,6-dimethoxybenzoquinone in 14 mL DMSO with 0.2 M Bu_4NBF_4 at room temperature under argon atmosphere.
[b)] NMR yields calculated after extraction with the addition of 1,3,5-trimethoxybenzene as an internal standard.
[c)] Without 0.2 M Bu_4NBF_4
[d)] With 3 equivalents of *p*-benzoquinone instead of 2,6-dimethoxybenzoquinone.

Table 3. Optimization of the electrolysis reaction of 1,2-octanediol.



Entry	Equivalent Benzoquinone	Equivalent of catalyst 1	Time [h]	Yield [%]	Recovered alcohol [%]	Charge [Coulomb]
1	0 equiv.	0.1 equiv.	7	21	73	9
2	0.25 equiv.	0.1 equiv.	7	63	26	68
3[a]	0.25 equiv.	0.1 equiv.	7	65	24	66
4	0.40 equiv.	0.1 equiv.	8	76	9	88
5	0.60 equiv.	0.1 equiv.	8	85	2	108
6	0.60 equiv.	0 equiv.	7	0	92	0
7	0.60 equiv.	0.01 equiv.	7	22	70	26
8	0.60 equiv.	0.05 equiv.	7	71	22	95
9[b]	0.40 equiv.	0.1 equiv.	8	71	11	98
10[c]	0.25 equiv.	0.1 equiv.	5	1	97	6
11[d]	0.25 equiv.	0.1 equiv.	4	6	90	6

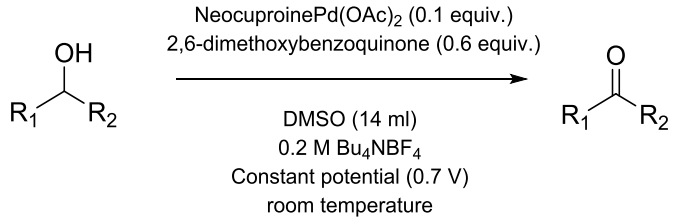
[a)] With 0.25 equivalents of *p*-benzoquinone instead of 2,6-dimethoxybenzoquinone, with a potential of 0.9 V instead of 0.7 V.

[b)] Electrolysis at 40 degrees Celsius.

[c)] With the addition of 0.1 M of Bu_4NOAc.

[d)] With the addition of 2 equivalents of Et_3N.

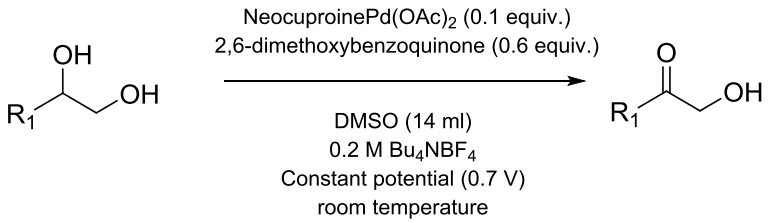
Table 4. Oxidation of singular alcohols.



Entry[a]	Alcohol	Potential (V)	Yield [%][b]	Recovered alcohol [%][b]	Charge [Coulomb]
1	1,2-octanediol	0,7	85	2	108
2	1-octanol	0,7	64	16	86
3	2-nonanol	0,7	8	90	3
4	1-nonanol	0,7	60	17	99
5	1-phenylethanol	0,7	10	85	2
6	benzylalcohol	0,7	60	25	72

[a)] reaction conditions: 0.7 mmol alcohol with 0.1 equivalents of neocuproinePd(OAc)$_2$ and 0.6 equivalents of 2,6-dimethoxybenzoquinone in 14 mL DMSO with 0.2 M Bu_4NBF_4 at room temperature with constant potential of 0.7 V for 8 hours under argon atmosphere.
[b)] NMR yields calculated after extraction with the addition of 1,3,5-trimethoxybenzene as an internal standard.

Table 5. Oxidation of diols.



Entry[a]	Alcohol	Potential (V)	Yield [%][b]	Recovered alcohol [%][b]	Charge [Coulomb]
1	1,2-octanediol	0,7	85	2	108
2	1,2-hexanediol	0,7	79	n.d.	95
3	1,2-decanediol	0,7	88	3	101
4	Cis-cyclohexanediol	0,7	57	n.d.	106
5	Trans-cyclohexanediol	0,7	58	n. d.	91

[a)] reaction conditions: 0.7 mmol alcohol with 0.1 equivalents of neocuproinePd(OAc)$_2$ and 0.6 equivalents of 2,6-dimethoxybenzoquinone in 14 mL DMSO with 0.2 M Bu_4NBF_4 at room temperature with constant potential of 0.7 V for 8 hours under argon atmosphere.

[b)] NMR yields calculated after extraction with the addition of 1,3,5-trimethoxybenzene as an internal standard.