Journal of Applied Electrochemistry (2005) 35:1265–1270
DOI 10.1007/s10800-005-9038-2

Evaluation of boron doped diamond electrodes for organic electrosynthesis on a preparative scale☆

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Received 20 December 2004; accepted in revised form 16 March 2005

Key words: biaryls, boron doped diamond electrodes, cleavage of C–C bonds, electrode stability, oxime reduction

Abstract

We have investigated some anodic and cathodic transformations using boron doped diamond (BDD) electrodes. The oxidation of a propargylic alcohol as well as the aromatic side chain oxidation in water as electrolyte did not yield the desired products in high yield and selectivity and led mainly to the formation of CO_2 due to electrochemical incineration of the starting material. With methanol as electrolyte, however, the reactivity of BDD electrodes is similar to graphite in most anodic methoxylation reactions, but the inactive behaviour of BDD electrodes leads to a different reaction pathway possibly involving methoxyl radicals with charge transfer from the electrolyte. It has been found that at BDD anodes benzylic single and double bonds can be split yielding aromatic acetals and esters. With phenanthrenes as starting material, *o,o′*-disubstituted biaryls were obtained. So the use of BDD electrodes provides an efficient and environmentally friendly access to this interesting class of compounds. The high H_2 overpotential of BDD cathodes enables smooth and selective reduction of functional groups like oximes. Due to the high chemical and mechanical stability of the diamond layer of today's electrodes, electrode lifetime as well as reproducibility of the electrosyntheses has improved markedly. Aqueous basic conditions, however, must be avoided for BDD anodes. These conditions result in degradation of the diamond surface.

1. Introduction

Boron doped diamond (BDD) electrodes are used for electrochemical incineration in wastewater treatment [1] due to their large overpotential for O_2 evolution. The latter allows also the production of inorganic peroxo compounds [2–5].

With regard to organic electrosyntheses on a preparative scale however, only few examples have been reported [5–9]. Selective transformations in aqueous electrolytes are difficult since complete degradation to carbon dioxide and/or unspecific formation of oxidation products like carboxylic acids are observed frequently [10]. To avoid CO_2 formation, low current densities ($i \ll 10$ mA cm^{-2}) have to be applied [5, 11]. With regard to space-time yield in electrochemical production, this is not satisfactory.

The production of hydroxyl radicals by water electrolysis on BDD anodes can be exploited for selective hydroxylation of the aromatic nucleus of salicylic acid [12]. Surprisingly, hydroxyl radicals generated by BDD anodes prefer attack on the 5-position of salicylic acid whereas hydroxyl radicals generated by Fenton reaction attack the 3-position. High yields of 2,5- or 2,3-dihydroxy benzoic acid could not be achieved due to further oxidation as an accompanying reaction [12].

We were able to show that for some examples reactivity of BDD anodes is similar to graphite anodes in direct methoxylations and indirect hydroxylations: *p-tert*-butylbenzaldehyde dimethylacetal is produced from *p-tert*-butyltoluene (TBT) in 65% yield [8, 13]. *p-tert*-butylbenzaldehyde (TBBA) is a starting material in fragrances and agro chemical production and is produced industrially by means of electrochemical methoxylation on graphite electrodes on a large scale [14]. Methoxylation of DMF also proceeds almost quantitative [6]. Cyclohexanone is hydroxylated in α position according to the method of Shono et al. [15] in an indirect electrolysis with iodide as the mediator in 89% yield [6]. Current densities of the last two reactions mentioned are 11 mA cm^{-2}; i.e. relatively low [6]. The hydroxylation product of cyclohexanone – 2-hydroxy cyclohexanone dimethyl acetal – can be further

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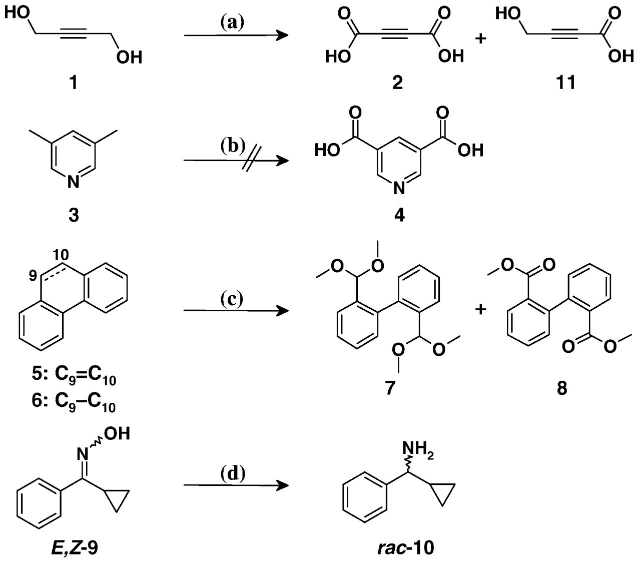
☆Dedicated to Professor G. Kreysa on the occasion of his 60th birthday.

transformed to cyclohexenone, a valuable intermediate e.g. for pharmaceuticals. We have previously reported that the central C–C single or double bond in bibenzyls and stilbenes can be cleaved selectively using BDD anodes and $MeOH/H_2SO_4/H_2O$ as the electrolyte [9].

With regard to cathodic reductions, BDD electrodes have a high overpotential for H_2 evolution by electrolysis in protic media [16]. For chemical transformations, BDD cathodes should behave like Pb or Hg cathodes.

We have investigated selected anodic and cathodic reactions in different reaction media. Anodic reactions in aqueous electrolyte like functional group conversions – of 2-butyne-1,4-diol **1** to acetylenedicarboxylic acid **2** – and aromatic side chain oxidations – of 3,5-dimethylpyridine **3** to pyridine-3,5-dicarboxylic acid **4** – did not yield the desired products in high yield and selectivity and resulted mainly in CO_2 formation (scheme 1).

Using a nonaqueous electrolyte e.g. methanol, the desired transformations like side chain oxidations [8], functional group conversions [6] and C–C bond cleavages [9] can be carried out selectively. Here we report the successful transfer of the concept of selective benzylic C–C bond cleavage on BDD anodes using a $MeOH/H_2SO_4/H_2O$ electrolyte to polynuclear arenes like phenanthrene **5** an 9,10-dihydrophenanthrene **6** as substrates. Cleavage of the C_9–C_{10} bond in these molecules gives *o,o′*-disubstituted biphenyls – diacetal **7** and diester **8** – which are interesting compounds for complex ligands exhibiting axial chirality (scheme 1, Figure 1).



Scheme 1. Overview of electrochemical reactions performed on a preparative scale using BDD electrodes. Reagents and conditions: (a) divided cell, BDD/Nb anode, electrolyte: 15% aq. H_2SO_4, 8 °C, 40 mA cm^{-2}, 11 h; (b) undivided cell, BDD/Si anode, 0.1 M aq. NaOH, 40 °C, 63 mA cm^{-2}, 34 h; (c) oxidation of **5**: undivided cell, BDD/Si anode, 0.5% H_2SO_4 in MeOH, 54 °C, 34 mA cm^{-2}, 3 h; oxidation of **6**: undivided cell, BDD/Si anode, 0.5% H_2SO_4 in MeOH, 54 °C, 34 mA cm^{-2}, 3 h; (d) divided cell, BDD/Nb cathode, 1% $NaOCH_3$ in anhydrous MeOH, 40 °C, 34 mA cm^{-2}, 4 h, 96% yield (by GC).

With regard to cathodic reductions, the chemoselective reduction of cyclopropyl phenylketone oxime **9** to *rac-C*-cyclopropyl benzylamine **10** was achieved with 96% yield on a BDD or Pb cathode using an anhydrous MeOH/NaOMe electrolyte in a divided plate and frame cell (scheme 1).

The reaction products were analysed and the surface of the electrodes after the reaction was studied.

2. Experimental details

2.1. *General*

BDD electrodes (CSEM Neuchâtel, Switzerland) for oxidation of **3**, **5** and **6** were prepared on a 10 cm diameter silicon substrate and BDD electrodes (Fraunhofer IST, Braunschweig, Germany) for oxidation of **1** and reduction of **9** were prepared on a 7×10 cm Nb substrate using the hot filament chemical vapour deposition (HF-CVD) technique. The concentration of the dopant in the gas phase was 1000 ppm (carrier concentration in BDD: $1{,}9\times10^{20}$ atoms cm^{-3}). All experiments were performed under galvanostatic conditions using undivided cells except the oxidation of **1** and reduction of **9**, which were carried out in a divided cell equipped with Nafion® 117 or 324 (DuPont, USA) membranes using a Gossen Konstanter 34GU60R5,5 rectifier. We have previously described the experimental setup for oxidation of **3**, **5** and **6** [8, 9]. NMR investigations were carried out with a Bruker Avance 400 MHz.

2.2. *Electrochemical oxidation in aqueous electrolyte*

Oxidation of 2-butyne-1,4-diol **1** (purchased from Acros) was carried out in a divided plate and frame cell equipped with a BDD/Nb anode, a Nafion® 324 membrane and a stainless steel cathode. A divided cell was used to avoid reduction of the triple bond of **1**. The anode/membrane and cathode/membrane distance was 7 mm each and the electrode surface was 35 cm^2. As anolyte, a mixture of 121 g water, 6.0 g (68.1 mmol) **1** and 23.4 g (240 mmol) H_2SO_4 (obtained from BASF) was employed. The catholyte was aqueous H_2SO_4 (15% by weight). The electrolytes were passed through the cell at a temperature of 8 °C and a current density of 40 mA cm^{-2} resulting in a cell voltage of 4–5 V. After application of 6 F per mol **1** (0.75 of the theoretical charge) electrolysis was stopped due to anodic gas production. The anodic off gas stream was passed through a aqueous $Ba(OH)_2$ solution resulting in precipitation of $BaCO_3$. Ethyl acetate extraction of the anolyte, $NaSO_4$ treatment of the combined organic layers and evaporation of the solvents yielded 1.5 g of a brownish oil. GC/MS analysis of this material after exhaustive silylation with MSTFA (trimethylsilyl methyl trifluoroacetamide) as the silylating agent showed the presence of unchanged **1** and hydroxymethyl propiolic acid **11** as the main products and traces of the desired

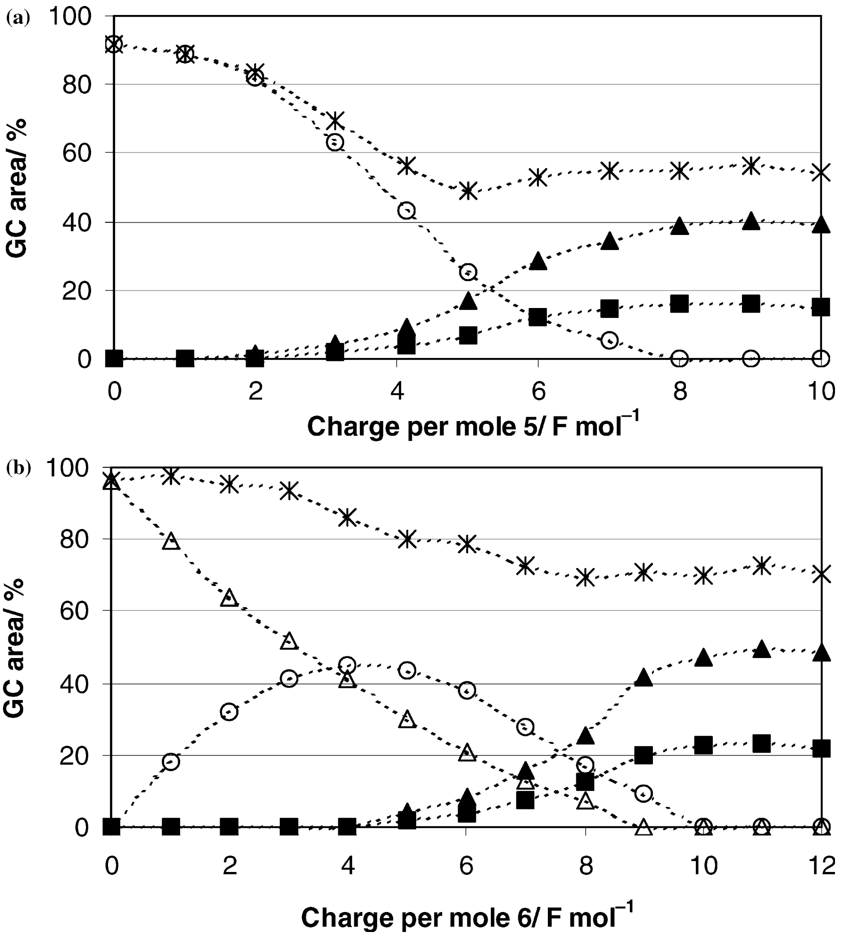


Fig. 1. Observed component concentration during oxidative cleavage of the C_9–C_{10} bond (qualitative GC % without solvent vs. charge consumed) in phenanthrene **5** (above) and 9,10-dihydrophenanthrene **6** (below) as determined by qualitative GC analysis. Legend: (△) indicates 9,10-dihydrophenanthrene **6**; (○) phenanthrene **5**; (■) diacetal **7**; (▲) diester **8**, and (*) the sum of the products obtained.

acetylene dicarboxylic acid **2**. The GC equipment employed was a hp 5880 A series GC System with a 30 m DB-1, 1.0 μm column which was operated with the following temperature program: 80°/5′/18°/300°. **1**, **2** and **11** were identified using GC/MS methods (Agilent MSD 5973) on their silylated derivatives: Trimethylsilyl (TMS) derivative of **1**: 1,4-bis-trimethylsilanyloxy-but-2-yne, $C_{10}H_{22}O_2Si_2$, $M_w = 230$ g mol^{-1}; TMS derivative of **2**: But-2-ynedioic acid ditrimethylsilyl ester, $C_{10}H_{18}O_4Si_2$, $M_w = 258$ g mol^{-1}; TMS derivative of **11**: 4-trimethylsilanyloxy-but-2-ynoic acid trimethylsilyl ester, $C_{10}H_{20}O_3Si_2$, $M_w = 244$ g mol^{-1}.

3,5-dimethylpyridine **3** (purchased from Aldrich) was oxidised in an undivided cell using a BDD/Si anode and a stainless steel cathode with an electrode surface of 63.6 cm^2 and an electrode distance of 3.4 mm. As electrolyte, a two phase mixture of 45.0 g (420 mmol) **3** and 405 g aqueous NaOH (0.1 M) was employed. Basic conditions were employed to avoid precipitation of the product. Electrolysis was carried out at a temperature of 40 °C and a current density of 63 mA cm^{-2}, giving a cell voltage between 4, 8 and 7 V. Electrolysis was carried out until 12 F per mol **3** (1.0 of the theoretical charge) were consumed. pH had to be adjusted during electrolysis since the electrolyte neutralized. The electrolyte was analysed using HPLC methods. Comparison with authentic pyridine-3,5-dicarboxylic acid **4** (purchased from Aldrich) showed that the starting material **3** was consumed but no diacid **3** was formed.

2.3. *Oxidation in nonaqueous electrolyte*

Oxidation of phenanthrene **5** as well as of 9,10-dihydrophenanthrene **6** was carried out in an undivided cell equipped with a BDD/Si anode and a stainless steel cathode. The electrode surface was 63.6 cm^2 and the electrode distance was 3.4 mm. For oxidation of **5**, an electrolyte consisting of 4.0 g (22.0 mmol) phenanthrene **5** (~90%, obtained from Fluka), 1.3 g H_2SO_4 (96% in H_2O, from BASF) and 245 g MeOH (from BASF) was electrolysed at a current density of 34 mA cm^{-2} and a temperature of 54 °C until a charge of 10 F per mol **5** (2.50 of the theoretical charge for formation of **7** and 1.25 of the theoretical charge for formation of **8**, respectively) was consumed. These conditions resulted in a cell voltage of ca. 6 V and gave 2,2′-bis-dimethoxymethyl-biphenyl **7** in 15% yield and biphenyl-2,2′-dicarboxylic acid dimethylester **8** in 39% yield by GC. Oxidation of **6** was carried out using an electrolyte consisting of 3.1 g 9,10-dihydrophenanthrene **6** (~94%, purchased from Aldrich) and 1.3 g H_2SO_4 (96%, from BASF) and 245 g MeOH (from BASF) was electrolysed under similar conditions as given above. Electrolysis was carried out until a charge of 12 F per mol **6** was consumed (2.00 of the theoretical charge for formation of **7** and 1.20 of the theoretical charge for formation of **8**, respectively). **7** was formed in 21% yield and **8** in 49% yield by GC.

The temporal evolution of the concentration of the products obtained during electrolysis was followed by qualitative gas chromatography using a hp 5880 A Series GC System with a 50 m Optima 1701, 0.25 μm column and is depicted in Figure 1. As temperature program, the following sequence was used: 40°/5′/5°/250°. The reaction media was neutralized using sodium bicarbonate (Riedel-de-Haën) before analysis. **7** and **8** as the reaction products were identified using GC/MS methods (Agilent MSD 5973) with **7** ($C_{18}H_{22}O_4$, $M_w = 302$ g mol^{-1}) and **8** ($C_{16}H_{14}O_4$, $M_w = 270$ g mol^{-1}) giving characteristic fragments for methyl esters and dimethyl acetals, respectively.

2.4. *Oxime reduction*

Reduction of cyclopropyl phenylketone oxime **9** to *rac*-*C*-cyclopropyl benzylamine **10** was carried out in a divided plate frame cell equipped with a BDD/Nb cathode, a Nafion® 117 membrane and a Sigraflex® 20010CI graphite anode (SGL Carbon, Wiesbaden, Germany) under exclusion of water to avoid hydrolysis of **9**. The anode/membrane and cathode/membrane distance was 7 mm each and the electrode surface 35 cm^2. As catholyte, a solution of 5.0 g (31.0 mmol) **9** (prepared by BASF following a known procedure [17]) and 3.3 g sodium methoxide solution (30% in methanol) in 91.7 g methanol was employed, whereas a solution of H_2SO_4 in methanol (2% by weight) was used as anolyte. Electrolysis was carried out at a current density of 34 mA cm^{-2}, a cell voltage between 10 and 14 V and a temperature of 40 °C until 6 F per mol **9** (1.50 of the theoretical charge) were consumed. GC analysis of the catholyte showed quantitative conversion of **9** to **10** with a selectivity of 96% and traces of *rac*-*C*-cyclopropyl *N*-methyl benzylamine as the only trace side product due to unwanted N-methylation of the product **10**. Cathodic H_2 evolution was indicating the end of the reaction.

Using a Pb cathode under the same reaction conditions was giving similar results. Work-up was performed by removal of the solvent in vacuum and methyl *tert*-butyl ether (MTBE) washing of the residual conductive salt. Filtration and evaporation of MTBE gave crude **10** as a red oil with a purity of >90%. Further purification can be carried out by distillation. **10** was identified by ^{1}H-NMR: (400 MHz, $CDCl_3$): $\delta = 0.29, 0.31, 0.41, 0.60$ (4m, 4×1H, cyclopropyl CH_2), 1.09 (m, 1H, cyclopropyl CH), 1.58 (s_{br}, 2H, NH_2), 3.18(d, $J = 10$ Hz, 1H, PhC*H*), 7.25 (m, 1H, *p*-PhH), 7.35, 7.41 (2m, 2× 2H, *m*-PhH, *o*-PhH).

With 2% H_2SO_4 as catholyte, reduction of **9** occurred slower and with lesser current efficiency and poorer selectivity with concurrent H_2 evolution from the beginning of reaction.

The temporal evolution of the concentration of the products obtained during electrolysis was followed by qualitative gas chromatography using a hp 5880 A Series GC System with a 30 m DB-1, 1.0 μm column. As temperature program, the following sequence was used: 50°/10′/10°/300°.

2.5. *BDD electrode stability*

The BDD electrode surfaces after being used as anodes under different conditions were investigated by scanning electron microscopy (SEM) with a Jeol 6400F (Figure 2). The electrode above was used in methanol and sulphuric acid as electrolyte. The micrograph shows the typical octahedral crystallite shape of the polycrystalline diamond layer. This material exhibits no sign of a morphological change. The electrode below was used for oxidation of 3,5-dimethylpyridine **3** in aqueous 0.1 M sodium hydroxide solution. The SEM image shows degradation of the surface due to oxidation of the diamond layer. The performance of this electrode

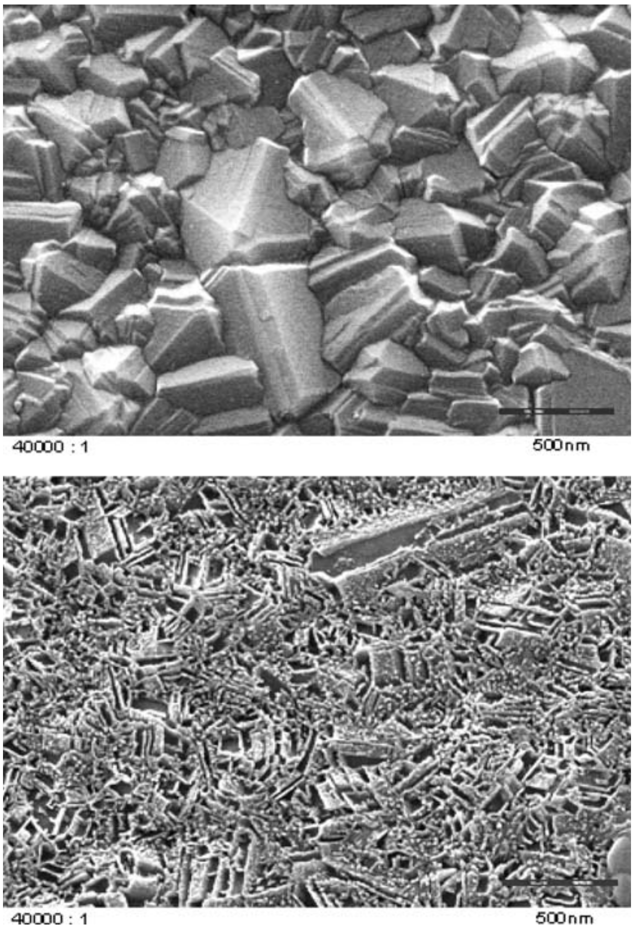


Fig. 2. SEM micrographs of a BDD/Si anode after electrolysis in MeOH/H_2SO_4 (above) and after attempted oxidation of **3** in 0.1 M aq. NaOH for 34 h (below).

however did not seem not to be influenced by this morphological change.

3. Results and discussion

3.1. *Electrochemical oxidation in aqueous electrolyte*

We investigated the electrochemical oxidation of 2-butyne-1,4-diol **1** to acetylenedicarboxylic acid **2** (an eight electron reaction) (scheme 1) and the attempted oxidation of 3,5-dimethylpyridine **3** to pyridine-3,5-dicarboxylic acid **4** (a 12 electron reaction) (scheme 1) using aqueous electrolytes. The latter was performed under basic conditions and as a consequence, changes in morphology of the diamond surfaces were observed (Figure 2). Since aqueous electrolytes were employed, reaction conditions led mainly to CO_2 formation due to complete oxidation of the starting material. The diacid **4** was not obtained; the diacid **2** was obtained in traces. The occurrence of hydroxymethyl propiolic acid **11** as intermediate by oxidation of 2-butyne-1,4-diol **1** shows that the oxidation occurs successively. The intermediate oxidation products of **2** in the course of total combustion to CO_2, however, need further elucidation.

Arene and propargylic side chain oxidation reactions to the corresponding acids are well known processes and can be carried out on PbO_2 or Ni(O)OH electrodes [18, 19] – typical electrodes for harsh oxidation conditions. BDD anodes, however, did not prove to be superior for selective oxidations with a high demand of charge in aqueous media. Electrolysis at relatively low current densities ($\sim$10 mA cm^{-2}) might be useful for this purpose but this results in unsatisfactory, and therefore, uneconomical space time yields.

3.2. *Oxidation in nonaqueous electrolyte*

The selective C–C bond cleavage in bibenzyls and stilbenes [9] was established as a new reaction principle (scheme 1, Figure 1). Reaction products are the corresponding acetals. C–C bond cleavage of phenanthrene **5** and 9,10-dihydrophenanthrene **6** gives *o,o′*-disubstituted biphenyls which are interesting compounds for chiral ligands exhibiting axial chirality. In this case, esters like the diester **8** and not the acetals are the main products. Oxidation of 9,10-dihydrophenanthrene **6** seems to proceed via phenanthrene **5** as intermediate probably by a methoxylation/elimination sequence (Figure 1). Figure 1 shows that the cleavage of the C–C_{10} bond in **6** proceeds more selective giving higher yields of **7** and **8**. The mechanism of conversion of **5** to **7** and **8** is not yet fully understood and its full elucidation limited by the poor solubility of **5** in methanol. The methoxylative cleavage of the C_9–C_{10} bond in **5** occurs probably by successive substitution with methoxy groups and/or addition of methoxy groups [9]. No biphenyls with mixed ester and acetal groups were formed.

To the authors knowledge, there is only one example for a selective electrochemical cleavage of the 9,10-bond in phenanthrene. Steckhahn and Kandzia report the use of an indirect electrosynthesis with the $PbO_2/IO_4^-/O{=}RuSiW_{11}O_{39}^{5-}$ system in a two phase electrolyte giving the *o,o′* biphenyl dialdehyde [20].

3.3. *Oxime reduction*

We have also investigated the reduction of oximes to amines on BDD cathodes. Hydrogenation of cyclopropylphenyl ketonoxime **9** to amine **10** proceeds under partial reduction of the cyclopropane subunit to propane. Oxime reduction on BDD cathodes in a divided cell proceeds chemoselectively in high yields. The methanolic alkaline electrolyte did not seem to attack the cathodic polarized BDD layer. In this case the BDD cathode showed similar electrochemical properties compared to lead or mercury cathodes, but with respect to toxicology, BDD cathodes are superior and no traces of heavy metals remain in the desired amine.

3.4. *Electrode stability*

The use of sulphuric acid in methanol provides an BDDE friendly electrolyte. Aqueous sodium hydroxide changes the morphology of the BDDE surface resulting in surface degradation (Figure 2) [21] but the electrode can still be used. Sodium methoxide in methanol does not significantly affect a BDD/Nb cathode. A BDD/Si cathode is not recommended for cathodic use due to the sensitivity of the Si layer under these conditions.

4. Summary and conclusion

The impression gained by the experiments performed is that organic electrochemical anodic transformations in MeOH at BDD electrodes are by far more selective than in water. The outcome of anodic methoxylation reactions is in some cases similar compared to graphite anodes. Different reaction pathways however led to products, which were not observed using graphite anodes. Careful investigation allowed us to develop a new protocol for the cleavage of benzylic C–C bonds under mild conditions [9].

The reaction mechanism at the interface BDD anode/MeOH was not been fully investigated.

Electrochemical reduction on BDD cathodes led to results comparable to mercury and led due to the high hydrogen overpotential. Even if used as cathodes, BDD electrodes have useful properties for preparative organic electrochemistry.

An aqueous basic electrolyte is not suitable for electrosyntheses with BDD anodes. Sodium methoxide in methanol however seems not to affect BDD/Nb cathodes.

In summary, BDD electrodes are a promising material for preparative organic electrochemistry.

Acknowledgements

Financial support from the BASF AG is gratefully acknowledged. The authors thank Philippe Rychen and Werner Haenni (CSEM SA) for helpful discussions, Heidrun Machwirth, Michaela Kimmel and Volker Steuer for technical assistance and Dr. Harald Winsel (all BASF AG) for providing oxime **9**.

References

1. M. Fryda, Th. Mathée, S. Mulcahy, M. Höfer, L. Schäfer and I. Tröster, *in* 'The Electrochemical Society Interface, Spring 2003', (2003), pp. 40–44 and references cited therein.
2. P.-A. Michaud, E. Mahé, W. Haenni, A. Perret and Ch. Comninellis, *Electrochem. Solid-St.* **3** (2000) 77.
3. L.J.J. Janssen and M.H.A. Blijlevens, *Electrochim. Acta* **48** (2003) 3959.
4. M.S. Saha, T. Furuta and Y. Nishiki, *Electrochem. Commun.* **6** (2004) 201.
5. P.-A. Michaud, Ch. Comninellis, W. Haenni, A. Perret, J. Niesta, M. Fryda and L. Schaefer, *in* 'Electrochemical Society Proceedings', Vol. 2001–23 (2003), pp. 87–96.
6. European Patent EP 1 036 861 B1 (BASF AG).
7. German Patent DE 103 13 169 A1 (Degussa AG).
8. D. Zollinger, U. Griesbach, H. Pütter and Ch. Comninellis, *Electrochem. Commun.* **6** (2004) 600.
9. D. Zollinger, U. Griesbach, H. Pütter and Ch. Comninellis, *Electrochem. Commun.* **6** (2004) 605.
10. P. Canizares, M. Diaz, J.A. Dominguez, J. Garcia-Gomez and M.A. Rodrigo, *Ind. Eng. Chem. Res.* **41** (2002) 4187.
11. J. Iniesta, P.-A. Michaud, M. Panizza and Ch. Comninellis, *Electrochem. Commun.* **3** (2001) 346.
12. B. Marselli, J. Garcia-Gomez, P.-A. Michaud, M.A. Rodrigo and Ch. Comninellis, *J. Electrochem. Soc.* **150** (2003) D79.
13. D. Zollinger, *Electrochemical Reactions at Diamond Electrodes in Aqueous and Non-aqueous Solutions Diploma* (Swiss Federal Institute of Technology, Lausanne, 2004) Diploma thesis.
14. P. Loyson, S. Grouws and B. Zeelie, *S. Afr. J. Chem.* **55** (2002) 125 and references cited therein.
15. T. Shono, Y. Matsumura, K. Inoue and F. Iwasaki, *J. Chem. Soc. Perkin Trans.* **I** (1986) 73.
16. H.B. Martin, A. Argoita, U. Landau, A.B. Anderson and J.C. Angus, *J. Electrochem. Soc.* **143** (1996) L133.
17. **9** was prepared by Friedel-Crafts acylation of benzene with 4-chloro-butyryl chloride (W.J. Close, J. Am. Chem. Soc. 79 (1957) 1455) followed by oximation (H.G.O. Becker, R. Beckert, G. Domschke, E. Fanghänel, W.D. Habicher, P. Metz, D.Pavel and K. Schwetlick, Organikum, Organisch-chemisches Grundpraktikum (Wiley-VCH, Weinheim, 2001), 675 pp).
18. (a) V. Wolf, Chem. Ber. 87 (1954) 668; (b) J. Kaulen and H.J. Schäfer, *Tetrahedron* **38** (1982) 3299.
19. US patent 5 002 641 (Reilly Industries, Inc.) and references cited therein.
20. E. Steckhahn and C. Kandzia, *Synlett* (1992) 139.
21. R. DeClements and G.M. Swain, *J. Electrochem. Soc.* **144** (1997) 856.