Electroreductive Deoxygenative C–H and C–C Bond Formation from Non-Derivatized Alcohols Fueled by Borohydride Oxidation

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Keywords: alcohols, borohydride, carboxylation, C–OH bond cleavage, electrochemistry

Abstract: Alcohols are one of the most common organic compound classes among natural and synthetic products. Thus, methods for direct removal of C–OH groups without the need for wasteful pre-functionalization are of great synthetic interest to unlock the full synthetic potential of the compound class. Herein, electroreductive C–OH bond activation and subsequent deoxygenative C–H and C–C bond formation of benzylic and propargylic alcohols is demonstrated. Experimental and theoretical studies indicate that the reductive C–OH bond cleavage furnishes an open shell intermediate that undergoes a radical-polar crossover to the corresponding carbanion that subsequently undergoes protonation to furnish alkane products. Furthermore, we demonstrate the carbanion can be trapped with CO_2 to form arylacetic acids, representing the first example of deoxygenative electrochemical C–C bond formation from non-derivatized alcohols. The cathodic transformations are efficiently balanced by the anodic oxidation of borohydride additives, a strategy that serves as a highly attractive alternative to the use of sacrificial metal anodes.

Introduction

Selective and efficient cleavage of covalent bonds to enable the formation of new bonds is a core feature of organic synthesis and of key importance for late-stage (de)functionalizations to provide compounds with new properties.[1,2] Alcohols represent a highly prevalent and versatile class of organic compounds, well represented among natural compounds as well as synthetic products with a wide range of structural complexity. As such, the abundant compound class is an important source of synthetic building blocks for a wide range of transformations. However, selective cleavage of the polarized C–OH σ-bond through either heterolytic or homolytic pathways is challenging. The low reactivity is reflected in the considerably higher bond dissociation energy (BDE) values compared to those of analogous polarized σ-bonds such as C(sp^3)–Br bonds (Figure 1, top left).[3,4] Traditional synthetic strategies to overcome the unfavored C–O bond cleavage relies on stoichiometric functionalization of the hydroxyl group into a better leaving group. Such derivatizations facilitate reductions, nucleophilic substitutions, transition metal–catalyzed cross-coupling reactions, etc., in both a two-electron polar setting and a radical manifold (Figure 1, top right).[5–9] For selective deletion of hydroxyl groups to furnish alkane products, the radical Barton-McCombie deoxygenation is still widely used, relying on derivatization of the alcohols to xanthate esters and stoichiometric use of chemical reductants such as tributyltin hydride or silanes.[10–12] In recent years, the pre-functionalization of alcohols into carboxylic esters, such as oxalate, toluate and benzoate, has gained attention as enabling strategy for deoxygenative transformations in a radical setting.[13–17] Similarly, in situ formation of activated alcohol derivatives using *e.g.* N-heterocyclic carbenes (NHC's) and phosphines is an efficient strategy in a single electron manifold.[18–22] While stoichiometric derivatization of the hydroxyl group has resulted in selective protocols for various transformations, the strategy is not ideal when considering atom and step economy. To tackle this, catalytic strategies for deoxygenative transformations of non-derivatized alcohols is an area of considerable synthetic interest that encompasses, *e.g.*, dehydrogenative transition metal catalysis,[23–26] catalytic Mitsunobu protocols,[27,28] carbocationic routes,[29–33] Tsuji-Trost type activation[34] and radical transition metal catalysis (Figure 1,

middle).[35,36] While often effective, these catalytic routes are associated with synthetic limitations as a result of their underlying mechanisms; dehydrogenative transformations and catalytic S_N2-type procedures are sensitive to steric hindrance, while ionic and radical routes require substrates that can stabilize the reactive intermediates. In the latter case, stoichiometric amounts of a terminal reductant are also required, commonly a metal powder such as Zn or Mn. For these reasons, the development of new general methods for C–OH bond cleavage without stoichiometric derivatization *in* or *ex situ* continues to be of great interest from a synthetic perspective. The topic has been highlighted as a key research area by the ACS Green Chemistry Institute Pharmaceutical Roundtable,[37] and has great potential for future applications in, *e.g.*, biomass valorization.

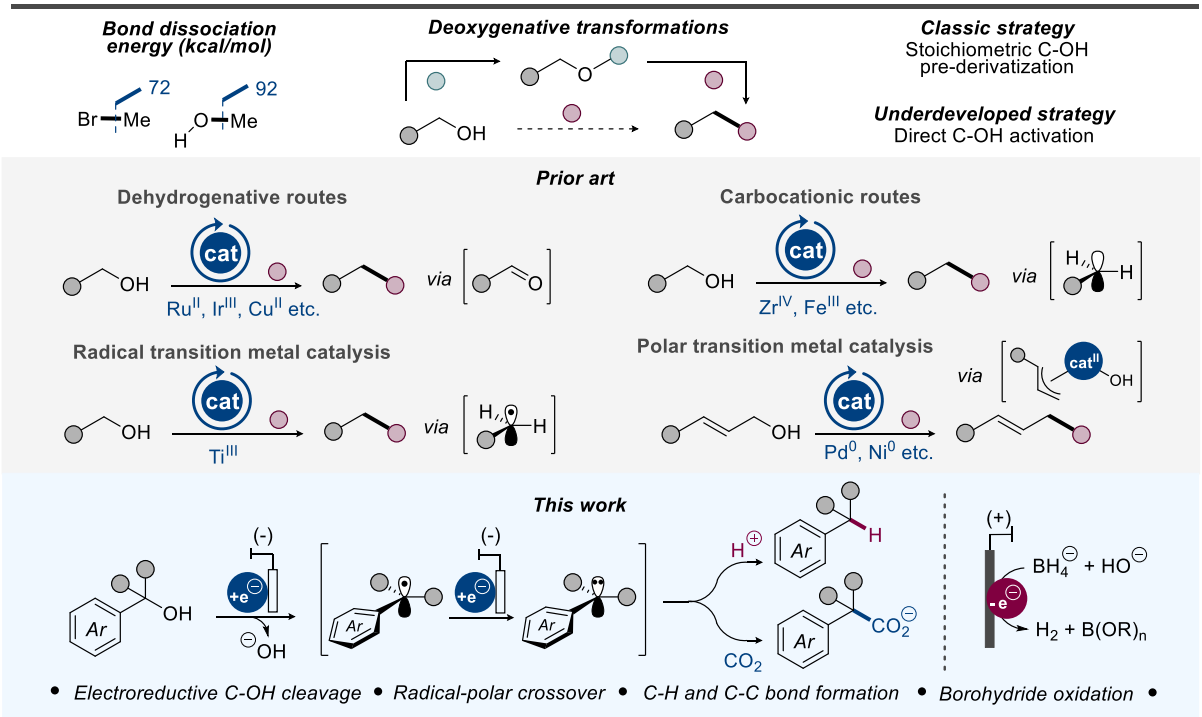


Figure 1. Routes for deoxygenative transformation of alcohols

Electrochemistry has become an increasingly popular synthetic approach to break and forge bonds in organic molecules in a radical setting, due to its inherent potential for new reactivity and selectivity as well as for resource-efficient synthesis.[38–44] In this context, electroreduction has proven to be a successful strategy for selective cleavage of polarized C–X σ-bonds in alkyl halides to furnish carbon-centered radical intermediates for a wide variety of applications,[45–48] including hydrodehalogenation of complex organic molecules[41] and cross-electrophile couplings.[49–53] In comparison, direct reduction of C–OH bonds requires significantly more negative potentials and only a handful of protocols have been reported in which the parent alcohol is not stoichiometrically derivatized *in* or *ex situ*.[54] To date, these protocols are limited to hydrodeoxygenation that furnishes alkane products. Given and Peover disclosed a protocol for electroreduction of xanthydrol to xanthene with phenol as a hydrogen source in 1959,[55] while the groups of Lund and Horányi demonstrated that electrochemical hydrodeoxygenation was viable for other π-activated alcohols under similar conditions in the following decades.[56–62] Electrochemical removal of allylic alcohols in taxoid structures was demonstrated by Commerçon and co-workers in 1994,[63–65] and Guo and co-workers recently disclosed a protocol for transformation of benzylic alcohols into the corresponding alkanes in the presence of $AlCl_3$ and a sacrificial aluminum anode.[66] In addition, electroreduction of allyl alcohol to propene and propane has been reported under acidic conditions.[60–62,67–70] It can be noted that, while deoxygenative bond formation to other atoms than hydrogen has been demonstrated under electrosynthetic conditions with alcohols as starting materials, these transformations rely on stoichiometric *in situ* derivatization of the hydroxyl group to *e.g.* esters,[71,72] carbonates,[73] phosphonium alkoxides[74–76] and borate esters.[77]

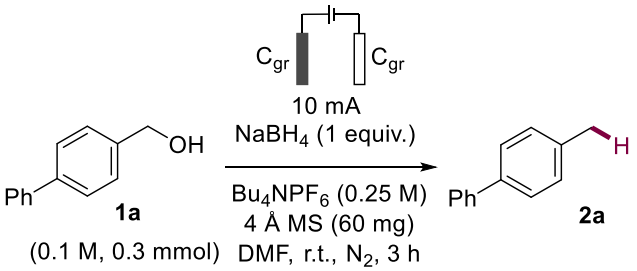
In electrosynthesis, the anodic and cathodic half-cell reactions must be designed to prevent starting materials, desired products or intermediate structures from undergoing unwanted side-reactions at the counter electrode. Such control over the redox reactions can be accomplished using divided cells or by judicious choice of a counter reaction that is more favored than side-reaction formation, thereby

enabling a user-friendly undivided cell setup. Electrooxidative transformations are commonly balanced by cathodic proton reduction for the formation of H_2, while electroreductive transformations have been balanced by oxidation of a variety of reductants including sacrificial metal anodes (*e.g.* Mg, Al or Zn). While this strategy is user-friendly for batch electrolysis on laboratory scale, it can be problematic for large scale processes and flow electrolysis due to the erosion of the anode that continuously changes the inter-electrode distance, results in the formation of inorganic salts that can cause cell blockages and the need for replacement within a relatively short timeframe.[78,79] As alternative, (super)stoichiometric use of additives, such as amines, phosphines, thioethers, and thioureas, has been demonstrated.[53,79] Furthermore, solvent oxidation has been used as the anodic counter reaction in aqueous and alcoholic systems, similar to their use in electrolyzer and fuel cell applications.[80,81] In context of the latter, borohydride reagents have been highlighted as an interesting reductant due to their low oxidation potentials.[82–84] Surprisingly, the use of such reagents is severely underdeveloped in an electrosynthetic setting. In two seminal papers, Huang and co-workers utilized sodium borohydride ($NaBH_4$) and tetrabutylammonium borohydride (Bu_4NBH_4) as additives to promote reductive cleavage of aryl ethers[85] and aryl fluorides.[86] While efficient, a drawback of these electroreductive transformations was the use of platinum electrodes as well as the lack of mechanistic detail. Inspired by Huang's work and leveraging the successful use of borohydride reagents in fuel cell applications, we demonstrate herein the use of borohydride reagents as fuel for the anodic counter reaction to promote electroreductive hydrodeoxygenation of benzylic and propargylic alcohols using inert carbon electrodes. In addition, we present the first examples of deoxygenative electroreductive C–C bond formation in the synthesis of arylacetic acids from non-derivatized alcohols and CO_2, along with mechanistic details of the processes.

RESULTS AND DISCUSSION

Initially, *p*-phenylbenzyl alcohol **1a** was chosen as the benchmark substrate for its electroreductive transformation into the corresponding alkane **2a** using graphite (C_{gr}) electrodes in an undivided cell with $NaBH_4$ as additive. Molecular sieves (MS) were added to the reaction to avoid hydrolysis of the borohydride (see Section 4.1 in the ESI), while the risk of overpressure from the anodic formation of H_2 was circumvented by ventilation of the reaction vessel with a continuous flow of N_2 through the headspace of the reaction. Under these conditions, the product alkane **2a** formed in 60% yield (Table 1, entry 1) after three hours, using one equivalent of $NaBH_4$ with respect to substrate **1a**. The beneficial effect of the borohydride reagent on the yield of the desired product was confirmed by a control reaction that resulted in a 36% yield of **2a** in its absence (Table 1, entry 2). The selectivity and yield for **2a** increased upon the addition of borohydride with an optimum at 0.3 equivalents (Table 1, entries 3-4), while increased borohydride loading resulted in a slower consumption of **1a** (Table 1, entry 5 and Section 4.2 in the ESI). A switch to Bu_4NBH_4 resulted in near quantitative yields of **2a** even after 2 h (Table 1, entry 6). Quantitative yields were also obtained using a lead cathode (Table 1, entry 7), whereas the use of other electrode materials as well as other solvents resulted in lower yields (see Sections 4.4 and 4.5 in the ESI). Excellent reproducibility was observed using either new graphite electrodes or electrodes cleaned with acid and subsequent sonication prior to reuse (see Section 1 and 3 in the ESI). Both lower and higher concentrations compared to the initial 0.1 M of **1a** resulted in lower yields of **2a** after 2 h (Table 1, entries 6 vs. 8–9), likely the result of by-product formation in the former case and incomplete conversion in the latter due to different amounts of charge/mol substrate transferred. Removal of the gas outlet, *i.e.* stopping the dynamic flow of N_2 through the reaction headspace, resulted in lower yields of **2a**, lower conversion of **1a** to products, and a less reproducible reaction (Table 1, entry 10). As expected, **2a** was not formed in the absence of current.

Table 1. Optimization for electroreductive hydrodeoxygenation of **1a**



Entry	Deviations from above	Yield **2a** (%)[a]	Conversion **1a** (%)[a]
1	none	60	61
2	no $NaBH_4$	36	86
3	0.1 equiv. $NaBH_4$	48	90
4	0.3 equiv. $NaBH_4$	65	87
5	0.5 equiv. $NaBH_4$	59	83
6	0.3 equiv. Bu_4NBH_4	94[b]	95[b]
7	0.3 equiv. Bu_4NBH_4, Pb (-)	95[c]	99[c]
8	0.05 M **1a**, 0.3 equiv. Bu_4NBH_4	61[b]	93[b]
9	0.15 M **1a**, 0.3 equiv. Bu_4NBH_4	71[b]	71[b]
10	no outlet	16	36
11	no current, 0.3 equiv. Bu_4NBH_4	0[b]	< 5[b]

[a] HPLC yield, see ESI for details [b] 2 h reaction time [c] 50 °C

With the optimized conditions at hand, a variety of alcohols were evaluated for the electrochemical hydrodeoxygenation (Figure 2). Selected primary, secondary, and tertiary benzylic alcohols were converted into the corresponding alkanes in high yields (**2a**–**2g**). Electron-donating groups such as alkyl chains and ethers were tolerated under the reaction conditions and resulted in products **2h**–**2l** in good yields. In contrast, the acetal-protected diphenol **2m** formed in mere 9% yield, whereas alkane **2o** with a free phenol failed to form (see Section 13 in the ESI). Interestingly, while aryl and methyl ethers (**2k**–**2l**) were stable under the applied conditions, benzylic ethers resulted in selective C–O bond cleavage at the benzylic position to furnish products **2b**, **2d**/**2ae** and **2af** in good yields. The hydrodeoxygenated thiophene and furan **2p** and **2q** formed in moderate to good yields, while substrates with basic heterocycles furnished only trace amounts of the expected products under the present condition (see ESI, Section 13). In addition, propargylic alcohols were converted into the corresponding alkene **2ag**

and alkane **2ah** in 10% and 53% yield, respectively. Benzylic substrates with electron-withdrawing substituents, such as nitriles and esters, were well tolerated under the reaction conditions, and *p*-cyanotoluene **2t** formed in good yield, as was its secondary counterpart **2u**. In contrast, sensitive benzylic cyanohydrin underwent side-reactions, and **2v** was observed in mere trace amounts when subjected to standard conditions. The ester-substituted **2w** formed in high yield from the corresponding alcohol, while the related alkane products **2x**, **2ab** and **2ac** formed in moderate yields. A slightly lower yield was obtained for methyl ketone **2ad**, being the result of carbonyl side-reactions (see Section 6 in the ESI). As expected from the trend in bond dissociation energy,[3,4] aromatic halides (Cl, F) were preferentially removed under the electroreductive conditions prior to cleavage of the C–OH bond. Hence, the formation of hydrodeoxygenation products **2y**–**2z** were not formed (see Section 13 in the ESI). Interestingly, introducing a cyano-group altered this preference and enabled the formation of alkane **2aa** in moderate yield with an intact C-F bond. This approach, however, was not sufficient to provide the deoxygenation product with the bromide analogue (see Section 13 in the ESI).

Under classic chemical Birch-type reduction of benzylic alcohols, the deoxygenative transformation is proposed to proceed via a benzylic carbanionic intermediate.[87–89] To probe this mechanistic hypothesis under our set of conditions, we set out to explore whether such an intermediate could be trapped with electrophiles other than protons. Our choice fell on carbon dioxide (CO_2), a well-established coupling partner for carbanions in the formation of carboxylic acids. Gratifyingly, a switch from an N_2 atmosphere to CO_2 enabled a selection of arylacetic acids to form, to the best of our knowledge, representing the first examples of deoxygenative C–C bond formation from non-derivatized alcohols under electrochemical conditions (Figure 3). The ester- and cyano-substituted phenylacetic acids **4w** and **4t** were isolated in 43% and 31% yield, respectively. In contrast, the tertiary cyano-substituted acid **4u** resulted in mere 3% yield, whereas tertiary alcohols failed to form the carboxylated products (see Section 13 in the ESI). Interestingly, the fluorinated analogue of *p*-cyanophenylacetic acid **4aa** was

obtained in a low yield (6%), whereas the fluorinated anti-inflammatory NSAID drug flurbiprofen **4ah** with an extended π-system was successfully isolated in 38%. In contrast, the primary non-fluorinated alcohol **1a** formed the carboxylation product **4a** in mere 4% yield while the electron-rich substrate **4a** failed to undergo cross-coupling (see Section 13 in the ESI for a list of all substrates assessed). In most cases, starting material remained at the end of the reaction and would not convert to product even upon extended reaction times or with additional borohydride.

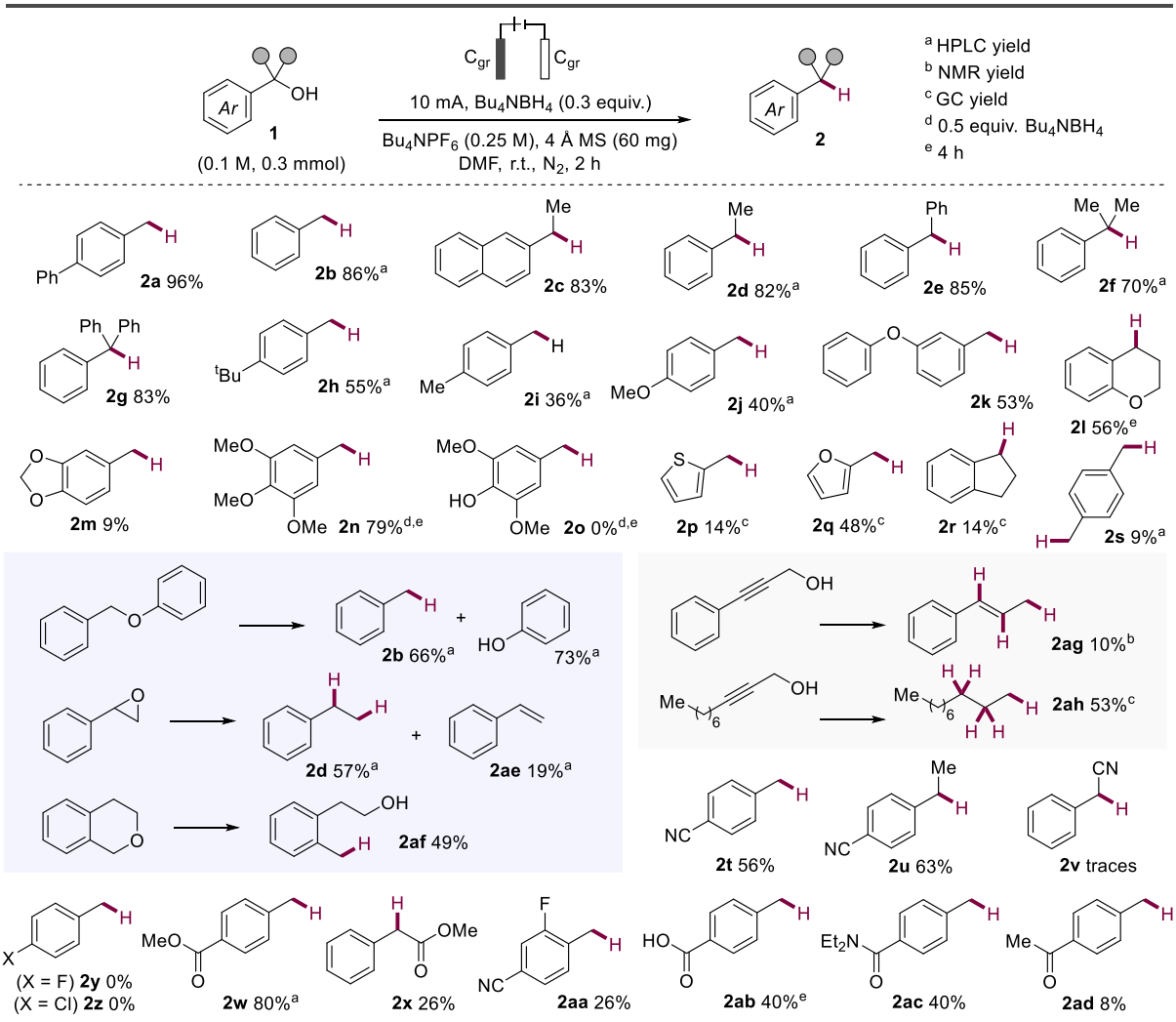


Figure 2. Substrate scope for electrochemical hydrodeoxygenation

To gain further insight into the aforementioned selectivities for the deoxygenative carboxylation we turned to density functional theory calculations (DFT) and cyclic voltammetry (CV) (see Sections 12 and 18 in the ESI for details). Notably, carboxylation products were only formed from alcohols with a calculated thermodynamic standard potential, E°, close to that of CO_2. In contrast, alcohols that failed to undergo electrocarboxylation displayed E° values significantly more negative compared to the coupling partner (Figure 3B). Furthermore, alcohols **1t** and **1w** that furnished arylacetic acids in good yields were found to have onset potentials less negative compared to that of CO_2 under the applied conditions (Figure 3B and ESI, Section 18). In contrast, alcohol **1a** with an onset potential almost identical to that of CO_2, formed carboxylation product in mere 4% yield, whereas alcohol **1n** that failed to form arylacetic acid **4n** had an onset potential more negative than that of CO_2. As such, the combined DFT and voltammetry data demonstrate that C–C bond formation occurs to a significant extent only when the radical/nucleophile precursor undergoes electron transfer prior to, or simultaneously as, the electrophilic cross-coupling partner, in line with what has previously been observed in other systems.[49,90] In the present case, considerably more negative standard potentials were determined by DFT for the reduction of the alcohols compared to their corresponding benzylic radical intermediates to carbanions (Figure 3B). This finding suggests that the radical-polar crossover is favored at the electrode surface once the open-shell intermediate forms. Hence, arylacetic acids are likely to form via carbanionic attack onto neutral CO_2 (see Section 12 in the ESI). Due to the continuously decreasing potential under the applied galvanostatic electrolysis conditions, such neutral CO_2 is expected to remain in solution in significant concentrations only in the presence of alcohols with a reduction potential less negative or similar to CO_2 itself. On the other hand, the small difference in reduction potential between the product-forming alcohols and CO_2 indicates that these species may be simultaneously reduced under the applied conditions and compete as electron acceptors (Figure 3B and Section 18, ESI). This notion is supported by the observed increase in reaction time required to afford full conversion of the alcohols in the presence of CO_2 (ESI, Section 8.2). As such, it cannot be ruled out that the C–C bond formation may also proceed via radical-radical coupling of benzylic open

shell intermediates and CO_2 radical anions (ESI, Section 12) and that the contribution of different pathways is substrate dependent. Likewise, it cannot be ruled out that CO_2 radical anions can act as reductive electron transfer mediators for certain substrates as reported for electroreduction of benzoate esters and thioethers.[16,91] It can be noted that alkyl carbonates were not observed in the reaction mixture by NMR, suggesting a distinctly different mechanism for the deoxygenative carboxylation compared to that reported by Senboku and co-workers.[73]

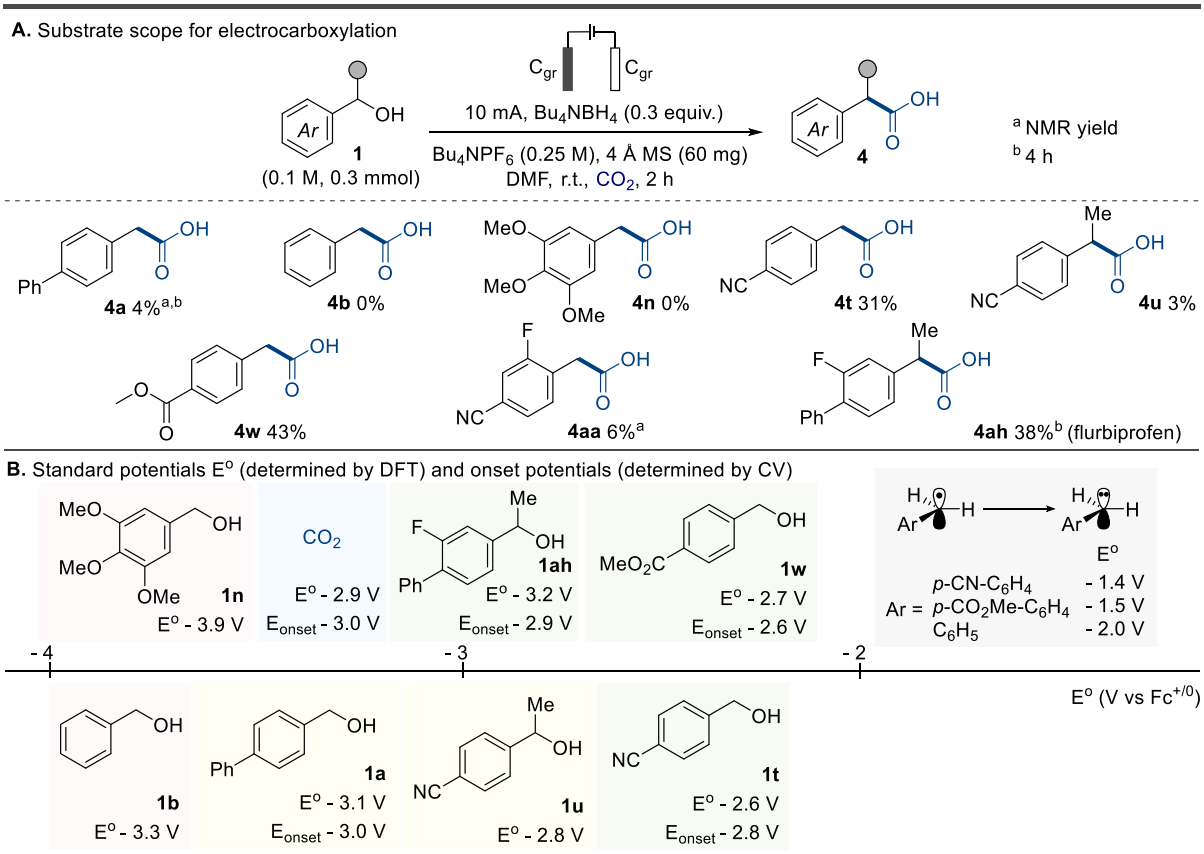


Figure 3. Electrocarboxylation of benzylic alcohols. A: Substrate scope. B: Standard and onset potentials (vs. $Fc^{+/0}$) for reduction of alcohols and CO_2 in DMF. Standard potentials were determined by DFT (ESI, Section 12) and onset potentials by CV (0.5 mM alcohol in 0.1 M Bu_4NPF_6 under Ar, WE: glassy carbon, CE: Pt-coil, reference electrode: SCE, sweep scan rate: 100 $mV \cdot s^{-1}$, for details see ESI, Section 18)

It is well established in fuel cell applications that borohydride compounds can undergo electrooxidation to generate H_2,[82–84,92,93] and bubble formation at the anode suggested that this is a likely path in the present system. Thus, hydride oxidation was hypothesized to act as the counter reaction to the electroreductive hydrodeoxygenation of study, thereby preventing oxidative formation of, *e.g.*, side-product **3a** (Figure 4A). Effectively, the hydride oxidation can be viewed as the inverse of cathodic proton reduction, a well-established counter reaction to electrooxidative transformations. The addition of sodium hydride improved the yield of **2a** significantly compared to the additive-free background reaction but was less efficient compared to the use of Bu_4NBH_4 as a reductant (Figure 4A). This difference suggested that the boron species generated upon borohydride electrooxidation may facilitate the deoxygenation via Lewis acid activation or boryl radical mediation, as reported under non-electrochemical conditions.[94–96] However, when a selection of boron compounds were added to the reaction mixture (Figure 4A), none of the additives except the benchmark borohydride reagent improved the yield of **2a** compared to the additive-free reaction, thus providing little support for this hypothesis. Recently, formation of borate esters intermediates between pinacolborane and alcohols were proposed in electrochemically driven deoxygenative borylation by Lin and co-workers.[77] Such borate ester intermediates may be envisioned to form also in the present system from electrooxidatively formed borane and alcohols or *in situ* formed aldehydes. Indeed, trialkylborate esters were found to furnish the desired alkane products upon electroreduction as indicated by DFT as well as electrolysis of pre-formed **5a** (Figure 4B and ESI, Sections 7 and 12). However, no improvements in yield were observed when BH_3·THF was used as additive in the reduction of **1a** compared to the additive-free background reaction (Figure 4A) and mere trace amounts of product **2a** were observed when aldehyde **3a** was used as substrate (Figure 4B). Furthermore, trialkylborate ester **5b** was not observed by ^{11}B-NMR when a crude reaction mixture from electrolysis of **1b** in d_7-DMF was analyzed halfway into the reaction (see Section 7 in the ESI). Finally, the borohydride reagent and graphite anode could be replaced with a sacrificial Zn anode for the reduction of **1a** to furnish **2a** in excellent yield (Figure 4B), demonstrating that boron compounds are not necessary for a successful

transformation. The combined experimental data, including the relatively forcing conditions required to synthesize benzylic trialkylborate esters (see Section 7 in ESI), in conjunction with the low barrier for C–O bond cleavage from the radical anion intermediate of the alcohol itself (Figure 4B), suggest that *in situ* formation and subsequent electroreduction of trialkylborate esters is unlikely to be the major mechanistic pathway in the present system. It can be noted that while C–O bond cleavage was facilitated in trialkylborate esters of π-activated alcohols, aliphatic analogues displayed lower standard potentials compared to their corresponding alcohols and failed as hydrodeoxygenation substrates (see Sections 7 and 12-13 in the ESI). As such, alcohol derivatization to borate esters does not appear to be a generally applicable strategy to promote deoxygenative transformations in a reductive one-electron setting.

A series of experiments were conducted to investigate the source of the proton in the hydrodeoxygenation products (Figure 4C). The use of d_7-DMF did not result in deuterium incorporation in the alkane product 2a, confirming that this solvent is a poor proton-donor.[97] Thus, the tetrabutylammonium cation of the supporting electrolyte and/or borohydride counterion appeared as a plausible source of protons via Hofmann elimination.[98,99] To probe this hypothesis, reactions were carried out using a supporting electrolyte unable of undergoing such elimination: KPF_6. Indeed, the use of this salt resulted in a significantly lower yield of product **2a** under otherwise identical conditions, suggesting that the tetrabutylammonium-based supporting electrolyte is not only enhancing the conductivity of the reaction medium under standard conditions but also acting as proton source. This conclusion was further supported by a reaction carried out with KPF_6 in the proton-donating solvent N-methylformamide (NMF) that restored the yield to a significant extent (Figure 4C).[98,99] Furthermore, a reaction using deuterated benzyl alcohol (**d-1b**) resulted in deuterium incorporation into product **2b**, thus demonstrating that hydroxyl protons may too act as hydrogen source in the present system. Similarly, the addition of d_4-methanol or d_3-MeCN resulted in a significant incorporation of deuterium

into product **2a**, in line with the reported proton donating abilities of these solvents.[98,99] Finally, the use of $NaBD_4$ resulted in deuterium incorporation into product **2a** to a minor extent, indicating that the borohydride may also serve as a hydrogen source. This route is likely to occur via H/D scrambling or via reduction of *in situ* formed **3a**.

Based on the combined experimental and theoretical data, we suggest a stepwise deoxygenation mechanism from the alcohol under standard reaction conditions (Figure 4D).[56,87] Initial cathodic single-electron reduction of the alcohol **1** results in a radical anion with the unpaired electron primarily residing in the *ipso*- and *para*-positions of the aromatic ring (for spin density calculations, see Section 12 in the ESI). Subsequent anionic C–OH bond cleavage results in a radical intermediate that rearomatizes to the benzylic radical **1'**. A second electron transfer results in a radical-polar crossover event and the formation of benzylic carbanion **1''** that undergoes protonation to furnish the alkane product **2** or undergoes coupling with CO_2 to form aryl acetic acid **4**. As anodic counter reaction, borohydride is oxidized to H_2 and boron-based side-products.

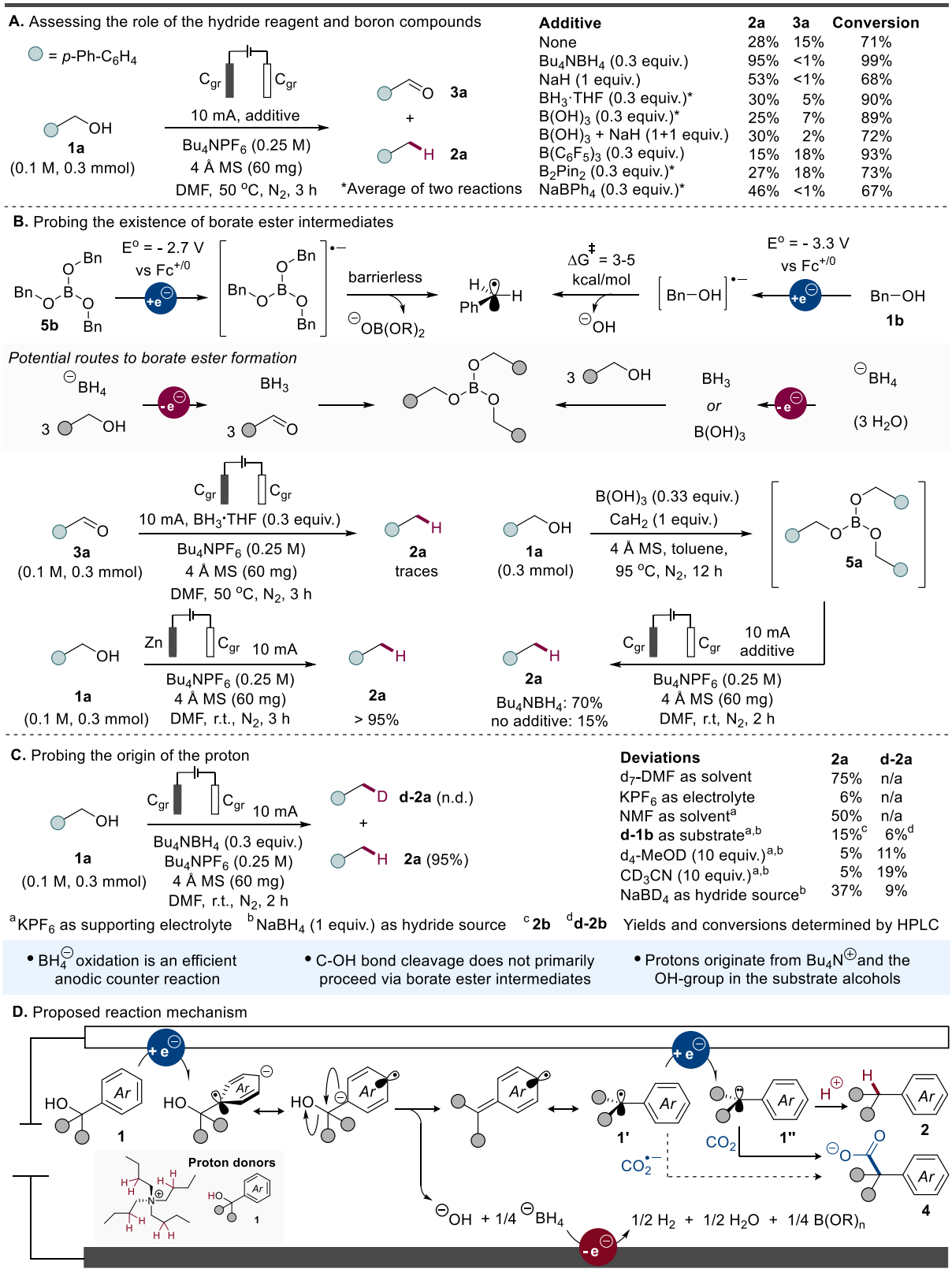


Figure 4. Mechanistic experiments. A: Assessment of hydride and boron compounds. B: Control reactions to probe the existence of borate ester intermediates (E° values and barriers obtained from

DFT, see ESI Section 12). C: Assessment of the proton origin. D: Mechanistic proposal for electroreductive deoxygenative transformations of alcohols.

Conclusions

The present work describes a protocol for direct electroreductive C–OH bond cleavage in non-derivatized π-activated alcohols to furnish alkanes and arylacetic acids, along with mechanistic details. The transformations leverage fuel cell technology by utilizing borohydrides as feedstock for the anodic counter reaction, thereby circumventing the need for sacrificial metal anodes. The anodic half-cell reaction results in H_2 formation and can, as such, be viewed as the inverse of the benchmark counter reaction for electrooxidative transformations - cathodic proton reduction. Experimental data suggest that the C–O bond cleavage occurs in the reduced alcohols rather than in borate esters formed *in situ* by the substrate alcohol and by-products from borohydride oxidation, a conclusion compatible with the results from DFT. At the operating potentials, the open-shell intermediates that result upon C-OH bond cleavage undergo a radical-polar crossover to the corresponding carbanions and furnishes alkanes in moderate to excellent yields upon protonation, primarily via Hofmann elimination of tetraalkylammonium ions. Alternatively, benzylic carbanions were possible to trap with CO_2 to furnish arylacetic acids in the first example of electrochemical deoxygenative C–C bond formation that proceeds with non-derivatized alcohols. Notably, successful coupling only took place when the reduction potential of CO_2 was similar to, or lower than, that of the alcohol as assessed by DFT and CV. This finding underscores the need to match the redox potentials of coupling partners for successful reaction outcome and highlights the utility of DFT and CV as predictive tools for desired reactivity in electrosynthesis. Due to the limited precedence for deoxygenative transformation of non-derivatized alcohols, the present work provides new insights that can enable their use in resource-efficient synthetic applications including upgrading of feedstock chemicals and late-stage derivatizations of organic compounds. Furthermore, borohydride oxidation is anticipated to find its use as anodic

counter reaction for a range of electroreductive transformations ahead to replace the use of sacrificial metal anodes in batch and flow electrolysis.

Acknowledgements

Financial support from the Swedish Research Council (grant no. 2021-05551), the Swedish Foundation for Strategic Research (grant no. FFL21-0005), Stiftelsen Olle Engkvist Byggmästare, Magnus Bergvalls stiftelse, Stiftelsen Lars Hiertas Minne, Frans Georg och Gull Liljenroths stiftelse and KTH Royal Institute of Technology is gratefully acknowledged. All calculations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at the PDC Centre for High-Performance Computing (PDC-HPC), the High-Performance Computing Center at Kungliga Tekniska Högskolan (KTH-PDC) in Stockholm through the project SNIC 2021/5-593, and the National Supercomputing Center under the project number SNIC 2021/5-591 and SNIC 2021/6-345 in Linköping, Sweden.

Supporting Information

The Supporting Information contains experimental procedures, screening data, DFT, and characterization data (spectroscopic, chromatographic and voltammetric).

Conflicts of Interest

The authors declare no competing financial interests.

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Original Draft, Writing – Review & Editing, Visualization, Supervision, Project administration, Funding aquisition. ‡These authors contributed equally.

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