EurJOC
European Journal of Organic Chemistry

Research Article
doi.org/10.1002/ejoc.202300220

Chemistry Europe
European Chemical Societies Publishing

www.eurjoc.org

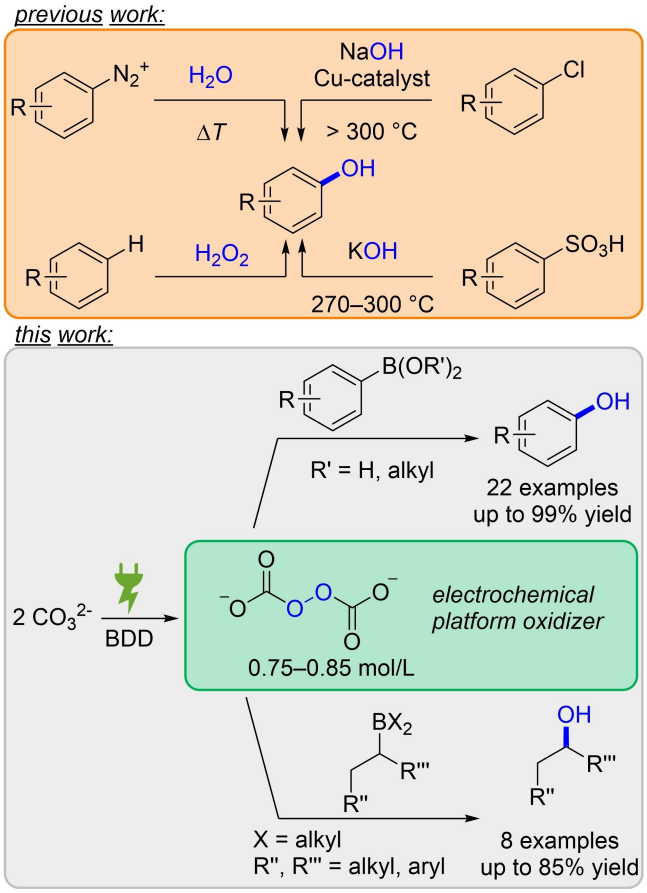
The Oxidation of Organo-Boron Compounds Using Electrochemically Generated Peroxodicarbonate

Philipp J. Kohlpaintner,[a] Lucas Marquart,[a] Lukas J. Gooßen,[b] and Siegfried R. Waldvogel*[a, c]

Peroxodicarbonate represents a green and largely underexplored oxidizer generated electrochemically from aqueous carbonate solutions. Through state-of-the-art electrolyzer technology, highly concentrated solutions have now become accessible. These were successfully employed as green oxidizer in deborolative hydroxylations. A plethora of phenols and alcohols have thus been synthesized in up to 99% from organoboron compounds using only green and non-toxic solvents. This transformation was successfully scaled-up to multi-gram batch sizes.

Introduction

Hydroxylated organic compounds such as phenols are an important class of molecules and are often encountered as synthetic intermediates,[1] natural products,[2,3] and active pharmaceutical ingredients.[4] The installation of these groups is often facilitated either via direct C–H oxidation[5,6] or the transformation of other moieties such as halides, sulfonic acids or diazonium salts under harsh conditions, often requiring metal catalysts (Scheme 1, top).[1] In direct comparison, the *ipso*-hydroxylation of boronic acids and their esters poses an attractive alternative, as these starting materials are widely available due to their wide-spread application in Suzuki–Miyaura cross-coupling reactions.[7–9] Arylboronic acids can be converted into the corresponding phenols by reaction with alkaline hydrogen peroxide (or it's adducts),[10,11] sodium perborate,[12] molecular oxygen,[13] *N*-oxides,[14] or hypervalent iodine compounds.[15] Similarly, the products of the hydroboration of alkenes can be converted to the respective alcohols.[10,11,15–18] However, these methodologies require the handling and storage of hazardous oxidizers and call for stoichiometric base equivalents to function properly. On the other hand, electrochemical methods pose an attractive potential alternative.[19–30] It allows conversion of organoboranes to the corresponding alcohols, but only in combination with the reduction of molecular oxygen in organic solvents,[31–33] thus imposing safety issues. Hence, we reasoned that an *ex-cell* generated "platform oxidizer" might circumvent the above-mentioned safety issues. The anodic production of high-performance oxidizers may turn out to be a key technology to defossilize chemical processes as it can be coupled to the industrial production of hydrogen from renewable sources



Scheme 1. Access to hydroxylated compounds.

[a] P. J. Kohlpaintner, L. Marquart, Prof. Dr. S. R. Waldvogel
Department of Chemistry, Johannes Gutenberg University Mainz
Duesbergweg 10–14, 55128 Mainz (Germany)
E-mail: waldvogel@uni-mainz.de
www.aksw.uni-mainz.de
[b] Prof. Dr. L. J. Gooßen
Evonik Chair of Organic Chemistry, Ruhr-University Bochum
Universitätsstraße 150, 44901 Bochum (Germany)
[c] Prof. Dr. S. R. Waldvogel
Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS-FMS)
Hermann-von-Helmholtz-Platz 1
76344 Eggenstein-Leopoldshafen (Germany)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202300220

Research Article
doi.org/10.1002/ejoc.202300220

(green hydrogen vs. blue hydrogen).[19] In general, electrochemistry can be considered a favorable alternative to conventional chemical processes as it is inherently safe and produces less waste.[19–23] It is already established in numerous applications such as dehydrogenative coupling reactions[34–36] and construction of heterocycles such as indazolinones,[37] pyrazoles/pyrazolines,[38] pyrazolidine-3,5-diones,[39,40] and benzoxazoles.[39,41–43]

(*Para*)periodate has recently been established as a high-performance platform oxidizer which can be generated at a boron-doped diamond anode.[44] It has been utilized in the contaminant-free syntheses of drug molecules such as levetiracetam and has great potential in pharmaceutical applications and direct access to elaborated building blocks.[45–47] The scaled production[48] and recycling in a self-cleaning process[49] provides increased sustainability.

In comparison, the use of peroxodicarbonate ($C_2O_6^{2-}$) is still largely under-explored. It can be generated via electrolysis from earth-abundant alkali carbonates (and thus by extension CO_2) and already carries base equivalents which can be exploited for synthetic applications.[50–55] Peroxodicarbonate is the dimer of carbonate that is generated by anodic oxidation of aqueous carbonate solutions at high current density and low temperature ($<5\,°C$). Recently, peroxodicarbonate was successfully synthesized in high concentrations of over 1.0 mol/L in an efficiently cooled cycled flow electrolysis at a BDD (boron-doped diamond) anode and high current density (>3 A/cm^2).[50] BDD is capable of transformations at very positive potentials and has an unusual durability.[56–60] This efficient synthetic entry is the prerequisite for elevating this oxidizer beyond the scope of an electrochemical curiosity. Newly found applications including the synthesis of amine *N*-oxides, sulfoxides, sulfones and epoxides led us to believe that one could harness the oxidative properties for many other synthetic transformations.[50,51] Herein, we report the *ipso*-hydroxylation of aryl-boronic acids and hydroxylation of double bonds using peroxodicarbonate as an electrochemically generated oxidizer as well as base equivalent, thus serving as a safer and sustainable alternative to other reagents (Scheme 1, bottom).

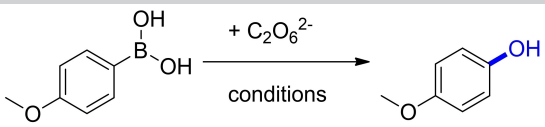
Results and Discussion

The starting point of this investigation was the direct oxidation of phenylboronic acids using peroxodicarbonate in aqueous organic solvents in analogy to our previous work on the oxidation of amines, sulfides and enones.[50,51] In order to determine the optimal reaction conditions for this transformation, we chose 4-methoxyphenyl boronic acid (**1 a**) as test substrate for our screening experiments. Noteworthily, a highly efficient electrosynthesis of peroxodicarbonate is already established,[50] producing batches of 35–75 mL with concentrations of up to 0.85 mol/L within 63–126 min, thus negating the need for tedious optimization.[61–63] This is an important advantage in addition to the versatility of this process.

To our delight, the reaction proceeded smoothly providing the desired phenol in 99% yield, as quantified by ^{1}H NMR with internal standard. Furthermore, we found that in this case – contrary to previous reports – only a slight excess (1.1 equiv.) of peroxodicarbonate solution was already sufficient to fully convert the starting material (Table 1). The oxidation of **1 a** occurs smoothly (table 1, entries 1 and 2) in various solvent systems (table 1, entries 4 and 7–8) with highest yields of **2 a** being obtained in ethanol and acetonitrile. In methanol, a slight decrease in yield was observed (Table 1, entry 8). Delightfully, the reaction even occurs in good yield if the boronic acid is added directly to the peroxodicarbonate solution without any additional solvent (Table 1, entry 9). This substantially simplifies the subsequent workup or downstream processing. The latter is usually the cost driver for the translation into technical application.[64] Increasing the amount of oxidizer to four equivalents drastically reduced the yield of the desired phenol, which infers that overoxidation or decomposition of the product occurs (Table 1, entry 6). Regrettably, it was not possible to identify the decomposition products. Due to the temperature sensitivity of peroxodicarbonate solution,[55] the yield decreases slightly when the reaction is carried out at ambient temperature, indicating that the decomposition of peroxodicarbonate becomes the predominant side reaction (Table 1, entry 5). Notably, no product formation was observed in a control reaction carried out in the absence of peroxodicarbonate (Table 1, entry 10).

With effective conditions at hand, we focused on applying the established conditions to a collection of aryl boronic acids. As all solvents screened in Table 1 showed similar yields by NMR, we decided to utilize green and less toxic ethanol as our primary solvent.[65,66] In order to ensure full conversion of the substrates, some oxidations were left to stir overnight, as no negative impact of overly long reaction times had been indicated in our reaction screening. The established conditions turned out to be suitable to convert several boronic acids into the respective phenols (Figure 1). Furthermore, it was possible to transform complex structures such as methylnaphthalene-,

Table 1. Screening experiments for the optimization of the *ipso*-hydroxylation of 4-methoxy-phenyl boronic acid (**1 a**).



1a **2a**

Entry	Solvent	equiv. $C_2O_6^{2-}$	Temp.	Time/h	Yield/%[a]
1	EtOH	1.5	0 °C to r.t.	16	99
2	EtOH	1.3	0 °C to r.t.	2	99
3	EtOH	1.1	0 °C to r.t.	1	53
4	EtOH	1.1	0 °C to r.t.	2	99
5	EtOH	1.1	r.t.	16	92
6	EtOH	4.0	0 °C to r.t.	16	30
7	MeCN	1.1	0 °C to r.t.	2	99
8	MeOH	1.1	0 °C to r.t.	2	95
9	EtOH	0.0	0 °C to r.t.	16	0
10	None[b]	1.1	0 °C to r.t.	16	95

[a] yield determined via ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard; [b] addition of peroxodicarbonate solution directly to pure 4-methoxy phenyl boronic acid.

Research Article
doi.org/10.1002/ejoc.202300220

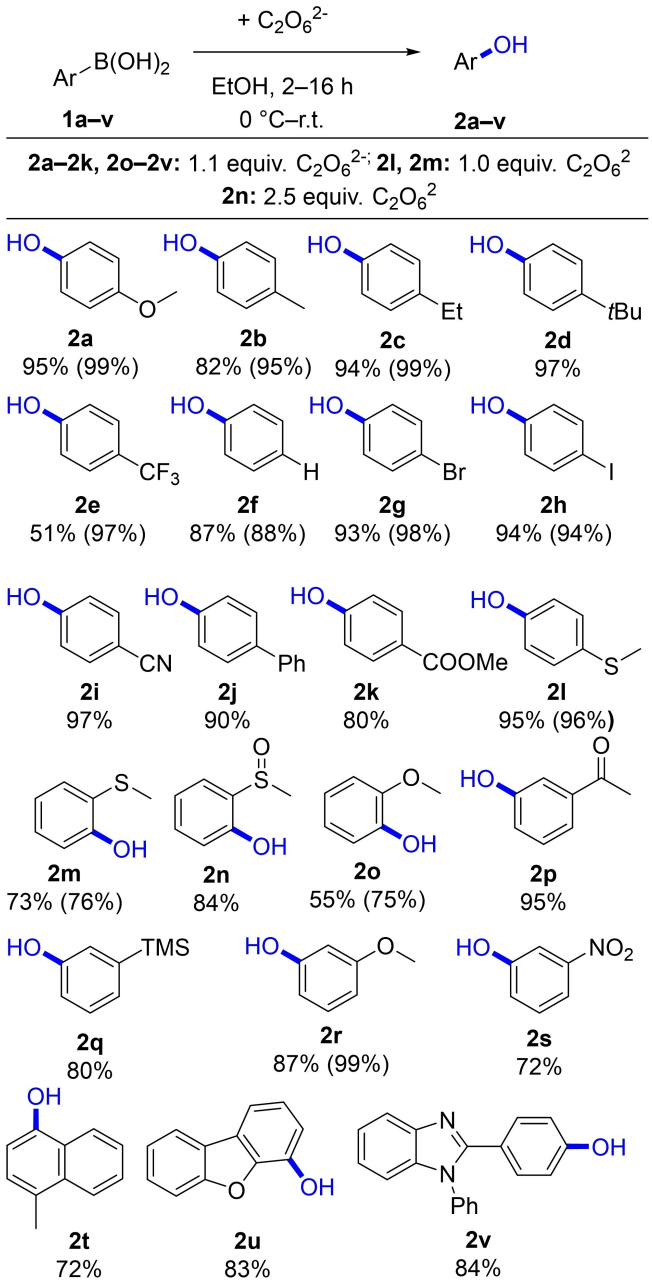


Figure 1. Scope of the *ipso*-hydroxylation using peroxodicarbonate. Numbers in parentheses denote ^{1}H NMR yields determined using 1,3,5-trimethoxy benzene as internal standard.

dibenzofuran-, and phenyl-benzimidazole-boronic acids in good to moderate yield (**2t**–**v**). This is in strong contrast to previous reports, in which solubility of the organic starting material was the key limitation.[50,51] Notably, the oxidation of *para*- and *meta*-substituted aryl boronic acids gives the desired phenols in better yield compared to the *ortho*-substituted starting materials. This becomes obvious when comparing the yields (both NMR and isolated) of the different methoxyphenols (**2a**, **2o**, and **2r**) as the NMR yields are 99% for the *para*- and *meta*-methoxy phenols and only 75% for the *ortho*-methoxyphenol.

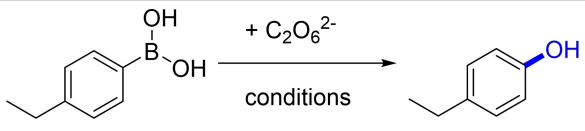
This is likely a result of the steric hindrance imposed by the neighboring group. In a similar fashion, the yield of the respective 2-(methylsulfanyl)phenol (**2m**) is lower than for **2l** (76% vs. 96%). Additionally, the 2-substituted derivative showed formation of the sulfoxide (**2n**) as byproduct. This was determined from the methyl shifts in the ^{1}H NMR (sulfoxide: $\delta =$ 2.96 ppm,[67] sulfide: $\delta = 2.33$ ppm,[68] both determined in $CDCl_3$) and GC-MS measurements. Thus, we investigated whether the sulfoxide could be obtained by selective over-oxidation. By increasing the amount of peroxodicarbonate to 2.5 equiv. we were successful in obtaining the respective 2-hydroxy sulfoxide (**2n**) in 81% isolated yield. In contrast, the *para*-substituted derivative **2l** underwent complete decomposition, when the amount of peroxodicarbonate was increased. Formation of the sulfone was only observed in <1% in both cases as was determined via GC-MS.

Our investigation also revealed that a variety of functional groups such as nitriles (**2i**), halogen substituents (**2g**–**h**), trimethylsilyl (**2q**), and esters (**2k**) are tolerated under the imposed alkaline conditions with little to no decomposition detected.

Over the course of these studies, we also explored the formation of phenols via the oxidation of pinacolboronate esters as alternative starting material. The oxidation of 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane under our established conditions gave the respective phenol **2f** in 94% yield. Additionally, scale-up reactions were attempted at both 30 mmol and 133 mmol scale (Table 2). For this, 4-ethyl boronic acid **1c** was transformed into the respective phenol **2c** in excellent yield (3.43 g, 94% and 16.09 g, 99%), thus providing clear evidence for the utility of peroxodicarbonate (Table 2). For the oxidation at 133 mmol scale, several electrolyzed peroxodicarbonate batches were added over time. Deviating from typical electrolysis conditions (2.1 h per 35 mL of electrolyte, corresponding to 10 *F* per mole of carbonate) the electrolysis batch was left running for 63 min before adding to the reaction mixture. This only lowers the overall concentration marginally (0.75–0.85 M vs 0.80–0.90 M) and increases the efficiency of the entire process dramatically.

For the mechanism, we propose one similar to the well-known mechanism for the hydroboration/oxidation with alka-

Table 2. Scale-up experiments for 4-ethylphenyl boronic acid (**1c**) to 4-ethylphenol (**2c**).



1c **2c**

Entry	Scale/mmol	*m* (phenol)/g	Isolated yield/%
1	3.0	0.33	90[a]
2	30.0	3.43	94[b]
3	133	16.09	99[b]

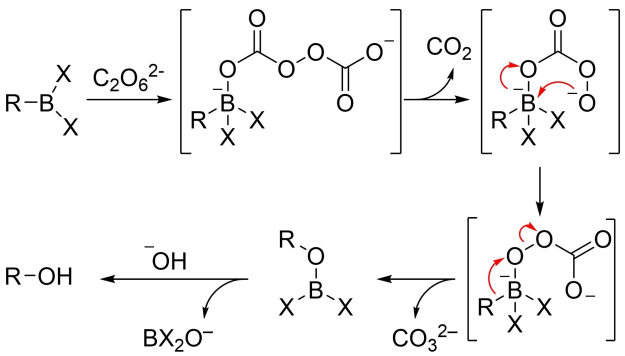
[a] purified using column chromatography; [b] purified via short-path distillation.

Research Article
doi.org/10.1002/ejoc.202300220

line hydrogen peroxide (Scheme 2). The organoborane is attacked by the charged end of the peroxodicarbonate molecule and subsequently releases CO_2, which is in turn trapped as bicarbonate under the alkaline conditions. Thereafter, the more nucleophile peroxidic part attacks the boron center in kind of Smiles-type rearrangement. The carbon moiety subsequently migrates to the oxygen atom releasing CO_3^{2-} and co-forming the boronic ester which might be subsequently hydrolyzed further under alkaline conditions. This mechanism also explains the absence of phenol during the reaction when using potassium trifluoro(phenyl) borate as starting material, which differs from the report of *Gupta* et al. using urea hydrogen peroxide.[10] In our case the negatively charged boron cannot be attacked by the peroxodicarbonate molecule.

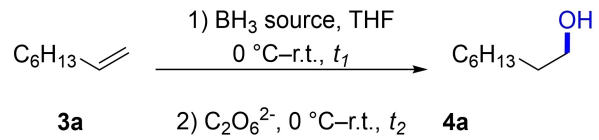
Over the course of these studies, we also investigated whether peroxodicarbonate can be utilized in a one-pot hydroboration-oxidation sequence of alkenes to the respective alcohols. Screening experiments were performed using oct-1-ene (**3a**) as test substrate in anhydrous THF. The yields were determined via an internal calibration using a commercial sample of octan-1-ol (**4a**) and decan-1-ol as internal standard (for further details see the Supporting Information). These findings are summarized in table 3. As becomes evident, the choice of hydroboration reagent does not affect the yield of **4a**. However, for simplicity reasons the hydroboration reagent of choice was deemed to be a 1 M BH_3·THF solution. Notably, the reaction did not proceed if no hydroboration reagent was present (Table 3, entry 14), whereas low conversion was observed when peroxodicarbonate was absent from the reaction. This is most likely attributed to oxidation occurring during GC sample preparation at ambient conditions (Table 3, entry 13). Furthermore, it was established that 0.8 equiv. of hydroboration reagent were necessary to facilitate full conversion to the respective alcohol **4a**. The reaction times were determined to be at least 4 h for the hydroboration and 2 h for the oxidation to the final product.

The alkenes were treated with 1 M BH_3·THF solution (0.8 equiv. per double bond, except for **4e** and **4f**) under argon atmosphere and subsequently oxidized directly with freshly prepared peroxodicarbonate solution. Using this simple one-pot hydroboration/oxidation protocol, several alkenes were therefore smoothly transformed in reasonable overall yields (Figure 2). In the case of myrtanol (**4e**), 0.9 equiv. of BH_3·THF solution were employed. For the synthesis of 1,5-cyclooctadiol (**4f**) commercial 9-BBN served as starting material. **4h** was prepared via two-fold oxidation of vinylphenyl-boronic acid by combining both the *ipso*-hydroxylation of aryl-boronic acids



Scheme 2. Postulated mechanism for the oxidation of organoboranes using peroxodicarbonate.

Table 3. Screening experiments for the hydroboration/oxidation of oct-1-ene **3a** to octan-1-ol **4a**.



Entry	BH_3 source (equiv.)	equiv. $C_2O_6^{2-}$	t_1/h	t_2/h	Yield/%[a]
1	$BH_3 \cdot Me_2S$ (0.8)	2.6	4	16	99
2	9-BBN (1.2)	2.7	4	16	99
3	1 m BH_3·THF (0.8)	2.6	4	16	99
4	1 m BH_3·THF (0.8)	2.6	1	16	81
5	1 m BH_3·THF (0.8)	2.6	3	16	95
6	1 m BH_3·THF (0.8)	2.6	5	16	99
7	1 m BH_3·THF (0.8)	2.6	16	1	99
8	1 m BH_3·THF (0.8)	2.6	16	2	99
9	1 m BH_3·THF (0.8)	2.6	4	1	91
10	1 m BH_3·THF (0.8)	2.6	4	2	99
11	1 m BH_3·THF (0.4)	1.5	4	1	78
12	1 m BH_3·THF (0.4)	1.5	4	2	93
13	1 m BH_3·THF (0.8)	0.0	16	0	21
14	None	2.6	–	2	0

[a] yield determined via GC using decan-1-ol as internal standard.

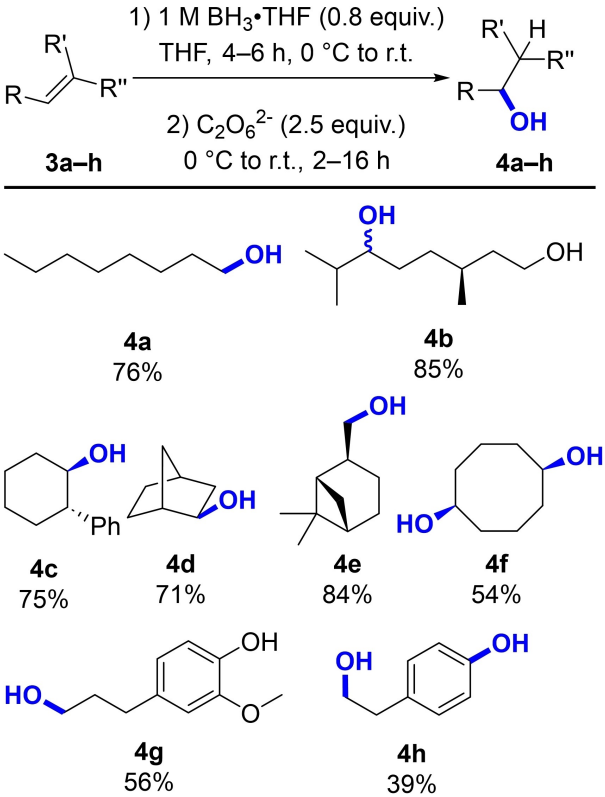


Figure 2. Scope of the hydroboration/oxidation sequence using peroxodicarbonate as oxidizer.

and the hydroboration/oxidation of an alkene. However, upon addition of hydroboration reagent the mixture became solid, thus decreasing the yield. The addition of mannitol (1.1 equiv.) and more THF improved the yield slightly, giving 39% of the product **4h**.

Conclusion

Electrochemically generated peroxodicarbonate was shown to be an effective and green oxidizing reagent for the deborolative oxidation of organo-boranes to the respective hydroxylated compounds. This way, phenols as well as aliphatic alcohols can be generated in good to almost quantitative yields. Thus, peroxodicarbonate serves as platform oxidizer and also provides the base equivalents required in the overall process. The simplicity thereof allows a scale-up beyond the decagram-scale in excellent yield (up to 99%). The reaction can optionally be performed in the absence of organic solvents, which is a particularly interesting feature for technical applications. Thus, this application markedly extends the applicability of the sustainable oxidizer peroxodicarbonate and further establishes it as a potential alternative to conventional, often expensive or hazardous methods. The successful conversion of 30 examples of aliphatic and aromatic organo-boron compounds underlines the versatility of this new method.

Experimental Section

General: All reactions concerning the *ipso*-hydroxylation of arenes were carried out at atmospheric conditions. Hydroboration protocols were performed under an argon atmosphere using oven-dried glassware and then reacted with peroxodicarbonate under atmospheric conditions. Solvents and reagents were commercially available and used without further purification. Cyclohexane (CH) and ethyl acetate (EA) were obtained in technical grade and purified via distillation. Anhydrous THF was obtained from a MB SPS-800 solvent purification system. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance III HD 400 (400 MHz). Chemical shifts δ are reported in parts-per-million (ppm) relative to the residual resonance in the deuterated solvent. Gas chromatography (GC) measurements were performed at a GC-2025 (Shimadzu, Japan) with a Zebron-5HT column (*Phenomenex*, U.S.A.). Dimensions of the column: 30 m·0.25 mm·0.25 μm. Carrier gas: hydrogen. GC-MS measurements were performed a GCMS-QP2010 SE (*Shimadzu*, Japan) with a VWR Avantor™ Highchrom HI-5MS column (*VWR International GmbH*, Germany). Dimensions of the column: 30 m·0.25 mm·0.25 μm. Carrier gas helium. Melting points were recorded using a Büchi M-656 apparatus (*Büchi*, Switzerland) with a heating rate of 1 °C/min and are uncorrected.

Electrochemical synthesis of peroxodicarbonate: A stock solution (2.25 M) of Na_2CO_3, K_2CO_3 and $KHCO_3$ was prepared according to the literature.[50] 35 mL of the electrolyte was then transferred to a Schott flask attached to the electrolyzer (for a more detailed description see the Supporting Information). The solution was then electrolyzed for either 63 min (corresponding to 5 *F*) or 126 min (corresponding to 10 *F*) at 0 °C and 3.33 A/cm^2. The amount of oxidizer generated was then determined using iodometric titration and used directly in the subsequent transformation.

Exemplary synthesis of 2a: To a cooled solution (ice-bath) of 4-methoxyphenyl boronic acid **1a** (307 mg, 2.02 mmol, 1.0 equiv.) in ethanol (10 mL) a freshly prepared solution of peroxodicarbonate (2.9 mL, 2,32 mmol, 1.1 equiv.) was added via glass pipette. The reaction was left for 4 h and acidified to pH 1 using 1 M HCl and extracted using ethyl acetate (3·20 mL). The combined organic fractions were then dried over anhydrous $MgSO_4$ and filtered. After removal of the volatiles *in vacuo*, the residue was submitted to either column chromatography (4:1, CH/EA) or bulb-to-bulb distillation (80 °C, 0.01 mbar) giving **2a** as a colorless solid. Yield: 236 mg, 1.901 mmol, 94%. $R_f = 0.24$ (4:1 CH/EA) Melting point: 54–56 °C; ^{1}H NMR (400 MHz), $CDCl_3$): $\delta = 6.83$–6.75 (m, 4H), 4.80 (s, 1H), 3.77 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 153.9$, 149.6, 116.2, 115.0, 56.0 ppm; GC-MS: $t_R = 7.73$ min (method "2_medium"), *m/z* for $C_7H_8O_2^+$ $[M]^+ = 124$.

Exemplary synthesis of 4a: In an oven-dried Schlenk flask, a solution of oct-1-ene, **3a** (0.4 mL, 2.53 mmol) in anhydrous THF was cooled with an ice-bath under argon atmosphere. A commercial 1 M BH_3·THF solution (2.0 mL, 2.0 mmol, 0.8 equiv.) was added slowly via syringe and the ice-bath removed afterwards. After 4 h the flask was cooled again with an ice-bath and a freshly prepared solution of peroxodicarbonate (7.9 mL, 2.5 equiv.) was added via pipette. The reaction was left stirring for 2 h and extracted with diethyl ether (3·25 mL). The combined extracts were then dried over anhydrous $MgSO_4$ and filtered. Removal of the volatiles *in vacuo* gave the crude product which was then purified via column chromatography (4:1; cyclohexane/ethyl acetate, $R_f = 0.22$) to give a colorless oil. Yield: 250 mg, 1.92 mmol, 76%). ^{1}H NMR (400 MHz), $CDCl_3$): $\delta = 3.63$ (t, $J = 6.7$ Hz, 2H), 1.55 (dt, $J = 7.9$, 6.4 Hz, 2H), 1.41 (d, $J = 5.8$ Hz, 1H), 1.37–1.24 (m, 10H), 0.92–0.84 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 63.2$, 32.9, 29.5, 29.4, 25.9, 22.8, 14.2 ppm; GC-MS: $t_R = 6.33$ min (method "2_medium"), *m/z* for $C_8H_{18}O^+$ $[M-OH]^+ = 112$.

Acknowledgements

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under FOR 2982/2–UNODE (WA1276/23-2) and Germany's Excellence Strategy–EXC-2033-390677874-RESOLV. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: alcohols · boron compounds · electrosynthesis · oxidation · peroxodicarbonate

[1] Z. Rappoport, *The Chemistry of Phenols*, Wiley, **2004**.
[2] J. H. P. Tyman, *Synthetic and Natural Phenols*, Elsevier, **1996**.
[3] L. Bravo, *Nutr. Rev.* **1998**, *56*, 317–333.

[4] K. A. Scott, P. B. Cox, J. T. Njardarson, *J. Med. Chem.* **2022**, *65*, 7044–7072.
[5] J. Börgel, L. Tanwar, F. Berger, T. Ritter, *J. Am. Chem. Soc.* **2018**, *140*, 16026–16031.
[6] R. Ullrich, M. Hofrichter, *Cell. Mol. Life Sci.* **2007**, *64*, 271–293.
[7] A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722–6737; *Angew. Chem.* **2011**, *123*, 6854–6869.
[8] N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, *20*, 3437–3440.
[9] N. Miyaura, A. Suzuki, *J. Chem. Soc. Chem. Commun.* **1979**, *0*, 866–867.
[10] S. Gupta, P. Chaudhary, V. Srivastava, J. Kandasamy, *Tetrahedron Lett.* **2016**, *57*, 2506–2510.
[11] G. W. Kabalka, P. P. Wadgaonkar, T. M. Shoup, *Organometallics* **1990**, *9*, 1316–1320.
[12] X. Yang, X. Jiang, W. Wang, Q. Yang, Y. Ma, K. Wang, *RSC Adv.* **2019**, *9*, 34529–34534.
[13] H. Kotoučová, I. Strnadová, M. Kovandová, J. Chudoba, H. Dvořáková, R. Cibulka, *Org. Biomol. Chem.* **2014**, *12*, 2137–2142.
[14] C. Zhu, R. Wang, J. R. Falck, *Org. Lett.* **2012**, *14*, 3494–3497.
[15] N. Chatterjee, A. Goswami, *Tetrahedron Lett.* **2015**, *56*, 1524–1527.
[16] H. C. Brown, G. Zweifel, *J. Am. Chem. Soc.* **1959**, *81*, 247–247.
[17] H. Brown, B. C. Rao, *J. Org. Chem.* **1957**, *22*, 1137–1138.
[18] R. S. Dhillon, *Hydroboration and Organic Synthesis: 9-Borabicyclo [3.3.1] Nonane (9-BBN)*, Springer, Berlin, Heidelberg, **2007**.
[19] D. Pollok, S. R. Waldvogel, *Chem. Sci.* **2020**, *11*, 12386–12400.
[20] A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2018**, *57*, 5594–5619; *Angew. Chem.* **2018**, *130*, 5694–5721.
[21] S. Möhle, M. Zirbes, E. Rodrigo, T. Gieshoff, A. Wiebe, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2018**, *57*, 6018–6041; *Angew. Chem.* **2018**, *130*, 6124–6149.
[22] M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230–13319.
[23] R. D. Little, *J. Org. Chem.* **2020**, *85*, 13375–13390.
[24] K. D. Moeller, *Chem. Rev.* **2018**, *118*, 4817–4833.
[25] C. Schotten, T. P. Nicholls, R. A. Bourne, N. Kapur, B. N. Nguyen, C. E. Willans, *Green Chem.* **2020**, *22*, 3358–3375.
[26] M. D. Kärkäs, *Chem. Soc. Rev.* **2018**, *47*, 5786–5865.
[27] R. D. Little, K. D. Moeller, *Chem. Rev.* **2018**, *118*, 4483–4484.
[28] C. Kingston, M. D. Palkowitz, Y. Takahira, J. C. Vantourout, B. K. Peters, Y. Kawamata, P. S. Baran, *Acc. Chem. Res.* **2020**, *53*, 72–83.
[29] M. C. Leech, K. Lam, *Nat. Chem. Rev.* **2022**, *6*, 275–286.
[30] A. Shatskiy, H. Lundberg, M. D. Kärkäs, *ChemElectroChem* **2019**, *6*, 4067–4092.
[31] K. Hosoi, Y. Kuriyama, S. Inagi, T. Fuchigami, *Chem. Commun.* **2010**, *46*, 1284–1286.
[32] J. Suzuki, N. Shida, S. Inagi, T. Fuchigami, *Electroanalysis* **2016**, *28*, 2797–2801.
[33] S. Inagi, T. Fuchigami, *Curr. Opin. Electrochem.* **2017**, *2*, 32–37.
[34] B. Dahms, P. J. Kohlpaintner, A. Wiebe, R. Breinbauer, D. Schollmeyer, S. R. Waldvogel, *Chem. Eur. J.* **2019**, *25*, 2713–2716.
[35] S. R. Waldvogel, S. Lips, M. Selt, B. Riehl, C. J. Kampf, *Chem. Rev.* **2018**, *118*, 6706–6765.
[36] J. L. Röckl, D. Pollok, R. Franke, S. R. Waldvogel, *Acc. Chem. Res.* **2020**, *53*, 45–61.
[37] J. C. Bieniek, M. Grünewald, J. Winter, D. Schollmeyer, S. R. Waldvogel, *Chem. Sci.* **2022**, *13*, 8180–8186.
[38] M. Linden, S. Hofmann, A. Herman, N. Ehler, R. M. Bär, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214820.
[39] T. Gieshoff, A. Kehl, D. Schollmeyer, K. D. Moeller, S. R. Waldvogel, *J. Am. Chem. Soc.* **2017**, *139*, 12317–12324.
[40] T. Gieshoff, D. Schollmeyer, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2016**, *55*, 9437–9440; *Angew. Chem.* **2016**, *128*, 9587–9590.
[41] T. Gieshoff, A. Kehl, D. Schollmeyer, K. D. Moeller, S. R. Waldvogel, *Chem. Commun.* **2017**, *53*, 2974–2977.
[42] O. Koleda, T. Broese, J. Noetzel, M. Roemelt, E. Suna, R. Francke, *J. Org. Chem.* **2017**, *82*, 11669–11681.
[43] L. Liu, Z. Xu, T. Liu, C. Xu, W. Zhang, X. Hua, F. Ling, W. Zhong, *J. Org. Chem.* **2022**, *87*, 11379–11386.
[44] S. Arndt, D. Weis, K. Donsbach, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2020**, *59*, 8036–8041; *Angew. Chem.* **2020**, *132*, 8112–8118.
[45] S. Arndt, B. Grill, H. Schwab, G. Steinkellner, U. Pogorevčnik, D. Weis, A. M. Nauth, K. Gruber, T. Opatz, K. Donsbach, S. R. Waldvogel, M. Winkler, *Green Chem.* **2021**, *23*, 388–395.
[46] S. Arndt, P. J. Kohlpaintner, K. Donsbach, S. R. Waldvogel, *Org. Process Res. Dev.* **2022**, *26*, 2564–2613.
[47] J. Klein, K. Alt, S. R. Waldvogel, *Adv. Sustainable Syst.* **2022**, *6*, 2100391.
[48] S. Arndt, R. Rücker, A. Stenglein, S. R. Waldvogel, *Org. Process Res. Dev.* **2022**, *26*, 2447–2455.
[49] C. M. Kisukuri, R. J.-R. Bednarz, C. Kampf, S. Arndt, S. R. Waldvogel, *ChemSusChem* **2022**, *15*, e202200874.
[50] A.-K. Seitz, P. J. Kohlpaintner, T. van Lingen, M. Dyga, F. Sprang, M. Zirbes, S. R. Waldvogel, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2022**, *61*, e202117563.
[51] A.-K. Seitz, T. van Lingen, M. Dyga, P. J. Kohlpaintner, S. R. Waldvogel, L. J. Gooßen, *Synlett* **2022**, *33*, 1527–1531.
[52] E. J. Ruiz-Ruiz, Y. Meas, R. Ortega-Borges, J. L. Jurado Baizabal, *Surf. Eng.* **2014**, *50*, 478–484.
[53] M. S. Saha, T. Furuta, Y. Nishiki, *Electrochem. Solid-State Lett.* **2003**, *6*, D5.
[54] M. S. Saha, T. Furuta, Y. Nishiki, *Electrochem. Commun.* **2004**, *6*, 201–204.
[55] C. P. Chardon, T. Matthée, R. Neuber, M. Fryda, C. Comninellis, *ChemistrySelect* **2017**, *2*, 1037–1040.
[56] Y. Einaga, *Acc. Chem. Res.* **2022**, *55*, 3605–3615.
[57] S. R. Waldvogel, S. Mentizi, A. Kirste, in *Radic. Synth. III* (Eds.: M. Heinrich, A. Gansäuer), Springer, Berlin, Heidelberg, **2012**, pp. 1–31.
[58] N. Yang, S. Yu, J. V. Macpherson, Y. Einaga, H. Zhao, G. Zhao, G. M. Swain, X. Jiang, *Chem. Soc. Rev.* **2019**, *48*, 157–204.
[59] Y. Einaga, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1752–1762.
[60] S. Lips, S. R. Waldvogel, *ChemElectroChem* **2019**, *6*, 1649–1660.
[61] M. Klein, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204140.
[62] S. B. Beil, D. Pollok, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2021**, *60*, 14750–14759; *Angew. Chem.* **2021**, *133*, 14874–14883.
[63] M. Dörr, M. M. Hielscher, J. Proppe, S. R. Waldvogel, *ChemElectroChem* **2021**, *8*, 2621–2629.
[64] J. Seidler, J. Strugatchi, T. Gärtner, S. R. Waldvogel, *MRS Energy Sustainability* **2021**, *7*, 42.
[65] K. Tekin, N. Hao, S. Karagoz, A. J. Ragauskas, *ChemSusChem* **2018**, *11*, 3559–3575.
[66] C. Capello, U. Fischer, K. Hungerbühler, *Green Chem.* **2007**, *9*, 927–934.
[67] S.-Y. Yao, X.-Y. Chen, Y.-L. Ou, B.-H. Ye, *Inorg. Chem.* **2017**, *56*, 878–885.
[68] M. L. Czyz, G. K. Weragoda, R. Monaghan, T. U. Connell, M. Brzozowski, A. D. Scully, J. Burton, D. W. Lupton, A. Polyzos, *Org. Biomol. Chem.* **2018**, *16*, 1543–1551.

Manuscript received: March 9, 2023
Revised manuscript received: March 13, 2023
Accepted manuscript online: March 14, 2023