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Organocatalyzed Anodic Oxidation of Aldehydes

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S *Supporting Information*

ABSTRACT: A method for the catalytic formation of electroauxiliaries and subsequent anodic oxidation has been developed. The process interfaces N-heterocyclic carbene-based organocatalysis with electro-organic synthesis to achieve direct oxidation of catalytically generated electroactive intermediates. We demonstrate the applicability of this method as a one-pot conversion of aldehydes to esters for a broad range of aldehyde and alcohol substrates. Furthermore, the anodic oxidation reactions are very clean, producing only H_2 gas as a result of cathodic reduction.

Electro-organic synthesis is a powerful yet underutilized method for effecting functional group interconversion. The advantages of bulk electrolysis, such as neutral reaction conditions, high chemoselectivities, and functional group polarity reversal (i.e., umpolung reactivity) have afforded significant enhancements to the existing arsenal of synthetic methods.[1] Much of the success in the area of electro-organic synthesis is owed to functional groups that serve as electro-auxiliaries, which can be chemoselectively oxidized or reduced under an applied potential to generate reactive intermediates.[1,2] While the electroauxiliaries provide high chemoselectivity, they also impose an inherent investment cost: their stoichiometric synthetic installation. Although rare, an elegant way to circumvent this challenge is to generate electroauxiliaries catalytically in situ.[3,4]

Inspired by the successful anodic oxidation of electron-rich alkenes (Figure 1),[1,4,5] we focused our attention on the Breslow
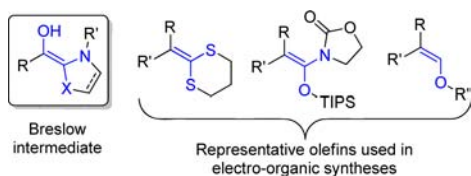

Figure 1. Generalized depiction of the Breslow intermediate (X = NR″, S) and comparison with structurally similar electron-rich alkenes used in anodic oxidations.

intermediate, which we viewed as a structural analogue that could be accessed via organocatalysis using N-heterocyclic carbene (NHC) catalysts and aldehyde substrates.[6] Notably, direct electrochemical oxidation of aldehydes can require high potentials (>2 V vs SCE).[3,7] In the presence of cyanide ion, the anode potential can be slightly less, presumably because of oxidation of a cyanohydrin intermediate, thus constituting an organocatalyzed anodic oxidation.[3,8]

Electrochemical studies of Breslow intermediates and related analogues have revealed low oxidation potentials (ca. −0.9 and −0.5 V vs SCE for the first and second oxidations, respectively),[9,10] which provides an opportunity for chemo-selective oxidations. Additionally, an electrochemical approach may balance anodic oxidations with cathodic reduction of H^+ to form H_2 gas, ultimately reaching the idealized efficiency expressed in eq 1.[1f,g]


$$\text{(1)}$$
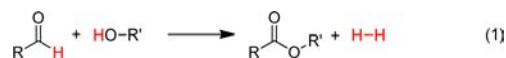
Despite investigations into the electrochemistry of the Breslow intermediate,[9,10] a *direct* electro-organic synthetic method using this species has not been realized. In general, bulk electrolyses of Breslow intermediates require an electro-chemical mediator.[10,11] This may be due in part to the challenges associated with outcompeting intermolecular homo-geneous reactions, such as benzoin condensation, with heterogeneous reactions at electrode surfaces. Additionally, low concentrations of catalytically generated electroactive intermediates limit the productive current flow during electrolysis.[1] Accordingly, NHC-catalyzed aldehyde oxidations have generally been accomplished using homogeneous oxidants, including azobenzene, quinones, 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO), N-chlorosuccinimide, and p-nitroaniline, or an excess of MnO_2.[12,13] In related "redox-transfer" reactions, α-functionalized aldehydes operate without external oxidants by balancing aldehyde oxidation with reduction at the α-position.[14] Herein we report the direct anodic oxidation of organocatalytically generated Breslow intermediates and demonstrate the utility of this method for the one-pot conversion of aldehydes to esters without the use of exogenous oxidants.

As depicted in Figure 2, we envisioned in situ formation of the Breslow intermediate followed by two-electron anodic oxidation to produce an electrophilic 2-acylazolium species. Nucleophilic attack from the alcohol would produce an ester with concomitant regeneration of the NHC catalyst. Oxidations at the anode would be balanced by the formation of H_2 gas at the cathode.

Our initial setup for bulk electrolysis of p-tolualdehyde involved using a three-neck round-bottom flask as an undivided cell, a reticulated vitreous carbon (RVC) anode, a Pt wire cathode, and Bu_4NClO_4 (0.045 M) as the supporting
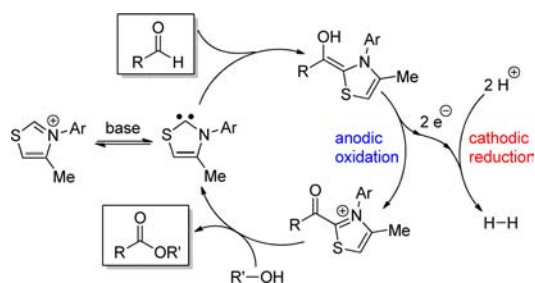
Figure 2. Proposed catalytic cycle for NHC-catalyzed anodic oxidation of aldehydes.

electrolyte. The cell potential was maintained at +0.1 V vs Ag/AgNO$_3$ (+0.4 V vs SCE). We found potentiostatic experiments to be more successful than using a constant current, which may be expected at low substrate concentrations.[1] Considering the propensity for competitive (hemi)acetal formation at high alcohol concentrations,[7,10] we introduced the alcohol (BnOH) in stoichiometric amounts relative to the aldehyde. Initial screenings revealed 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and CH$_3$CN to be an optimal base and solvent combination (the use of tetrahydrofuran, dimethoxyethane, dimethyl sulfoxide, and N,N-dimethylformamide as solvents gave similar results).

An initial catalyst screen indicated that thiazolylidines were more effective than their imidazolylidine, triazolylidine, and acyclic diaminocarbene counterparts. We speculate that the better performance of the thiazolylidine-derived catalysts may be attributed to more favorable access to the Breslow intermediate in comparison with NHCs bearing an additional ring substituent at the 1-position (i.e., NR in place of S). Although the observation of aldehyde-derived Breslow intermediates remains challenging,[9] it is expected that those comprising thiazoles would encounter less A^{1,3} strain than those derived from classes of NHCs bearing additional exocyclic substituents.

Under our initial conditions, oxidation of p-tolualdehyde proceeded in 46% yield after 48 h using 10 mol % 4-methyl-3-(2,4,6-trimethylphenyl)thiazolium perchlorate as a precatalyst. Analysis of the product mixture revealed a significant amount of benzil-type product. Notably, aerobic oxidation of benzoins is catalyzed by NHC/DBU combinations, presumably proceeding through the corresponding enol(ate) of the benzoin species.[15] Interestingly, under a N$_2$ atmosphere and without an applied cell potential, we still observed benzil products. Further experiments indicated perchlorate to be the culprit oxidant. Changing the electrolyte to Bu$_4$NBr (TBAB) and the thiazolium counterion to tetrafluoroborate improved the yield of the ester to 94% after 48 h. The benzoin-type product was still observed by ^{1}H NMR spectroscopy but was confirmed to be equilibrating under the reaction conditions [see the Supporting Information (SI)].

Electrode materials and dimensions are an important consideration in bulk electrolyses.[1] Increasing the surface area of the counter electrode from Pt wire (ca. 7.2 cm^2) to a Pt basket (ca. 20 cm^2) gave nearly quantitative formation of the desired ester after 17 h. Excellent yields were maintained when the RVC anode (surface area = 40 cm^2) was replaced with an inexpensive graphite drawing stick (0.6 cm × 0.6 cm × 7.5 cm, submerged surface area = 4.5 cm^2). We observed gas formation at the cathode consistent with the production of H$_2$, as expected considering the low hydrogen overvoltage of the Pt

cathode.[1f,g] This mechanistic detail was further confirmed by trapping of the gas formed in the headspace of the electrochemical cell with Vaska's complex to form the corresponding dihydride (see the SI).[16] Using a carbon cathode in place of Pt resulted in decreased reaction efficiency. Notably, no ester production was observed in the absence of the thiazolium precatalyst or DBU.

We next focused on the scope of the aldehyde and alcohol substrates; key data are summarized in Table 1. In general, good to excellent yields were obtained for most aldehydes. Substitution at the ortho position was tolerated (entries 2 and 3), and excellent chemoselectivity was observed in the presence of electrophilic groups such as carboxylic acid (entry 4), cyano (entries 5 and 6), and ester (entry 26) functionalities. Other electron-deficient benzaldehydes were also viable, such as 4-fluoro-, 4-chloro-, and 4-bromobenzaldehyde (entries 7−9, respectively). In general, in the presence of an N-(2,4,6-trimethylphenyl)-substituted catalyst, electron-deficient aldehydes displayed an increased extent of benzoin formation that severely inhibited efficient ester production. The increased electrophilicity of the aldehydes, however, permitted the use of a bulkier NHC catalyst. Specifically, the N-(2,4-diisopropylphenyl)-substituted analogue shepherded reactivity away from benzoin condensation and furnished high yields of ester products in short reaction times. Not surprisingly, 4-nitrobenzaldehyde yielded a mixture of products containing only ca. 10% of the desired ester, likely due to reductive coupling of the nitroarene.[12l,17]

Although anodic oxidation of the electron-rich heteroaromatic 2-furfural proceeded in good yield (97%; Table 1, entry 12), electron-rich benzaldehydes such as 4-methoxy- and 4-dimethylaminobenzaldehyde were sluggish to react even at elevated temperatures. These latter results are consistent with other approaches to NHC-catalyzed oxidation of electron-rich benzaldehydes that are considered deactivated toward formation of the Breslow intermediate.[10,12] Moving the electron-donating group out of conjugation with the aldehyde (i.e., 3-anisaldehyde; entry 13) restored the reactivity, and the desired ester was obtained in 87% isolated yield.

Oxidation of nonaromatic cyclohexanecarboxaldehyde also proceeded smoothly (Table 1, entry 14), as did oxidation of α,β-unsaturated cinnamaldehyde and 4-methoxycinnamaldehyde (entries 15 and 16, respectively). This latter substrate class indicated to us that the electrochemical oxidation of the Breslow intermediate is sufficiently rapid to avoid competitive reaction pathways such as Stetter reactions, lactone formation, and conjugate reduction.[14,18]

A range of alcohols were found to be compatible (Table 1, entries 17−26). As expected, s-BuOH (entry 19) displayed lower reactivity than did primary alcohols, and no ester product was obtained when t-BuOH was employed (entry 20). Functionalized and activated alcohols such as benzyl alcohol, allyl alcohol, propargyl alcohol, 4-pentyn-1-ol, and 2-(trimethylsilyl)ethanol furnished the corresponding esters in good to excellent yields.

To improve the overall practicality of the organocatalyzed anodic oxidations, we considered replacing the potentiostat with a simple battery, similar to what has been demonstrated for constant-current oxidations.[19] Our initial conditions involved the oxidation of p-tolualdehyde to benzyl toluate using a two-electrode setup driven by commercial batteries (Table 2). Use of a 6 V lantern battery (entry 1) failed to produce the ester product, possibly because of destructive

Table 1. Substrate Scope of NHC-Catalyzed Anodic Oxidation of Aldehydes[a]

entry	R	R'	Ar	time (h)[b]	FE (%)[c]	yield (%)[d]
1	4-MeC$_6$H$_4$	Bn	Mes	17	74	98 (97)
2	2,4-Me$_2$C$_6$H$_3$	Bn	Mes	22	91	94 (93)
3	2,4-Cl$_2$C$_6$H$_3$	Bn	DiPP	7	93	91
4	4-CO$_2$HC$_6$H$_4$	Bn	Mes	15	49	97
5	4-CNC$_6$H$_4$	Bn	DiPP	2	99	65
6	3-CNC$_6$H$_4$	Bn	DiPP	6	91	94
7	4-FlC$_6$H$_4$	Bn	Mes	14	82	97 (92)
8	4-ClC$_6$H$_4$	Bn	DiPP	8	98	98
9	4-BrC$_6$H$_4$	Bn	DiPP	8	94	98
10	4-IC$_6$H$_4$	Bn	DiPP	7	83	88
11	2-pyr	Me	DiPP	4	83	71 (60)
12	2-fur	Bn	Mes	5	92	97 (91)
13	3-MeOC$_6$H$_4$	Bn	Mes	11	97	92 (87)
14	cyclohexyl	Bn	Mes	56	99	87 (85)
15	cinnamyl	Bn	Mes	7	99	90 (83)
16	4-MeO-cinnamyl	Bn	Mes	27	72	98
17	4-MeC$_6$H$_4$	Et	Mes	12	70	98 (95)
18	4-MeC$_6$H$_4$	2-PhEt	Mes	36	50	72 (70)
19[e]	4-MeC$_6$H$_4$	s-Bu	Mes	24	97	45
20	4-MeC$_6$H$_4$	t-Bu	Mes	4	0	0
21	4-MeC$_6$H$_4$	allyl	Mes	36	49	72 (66)
22	2,4-Me$_2$C$_6$H$_3$	allyl	Mes	13	91	91 (83)
23	4-MeC$_6$H$_4$	propargyl	Mes	13	97	96 (89)
24	4-MeC$_6$H$_4$	4-pentynyl	Mes	25	85	88 (74)
25	4-MeC$_6$H$_4$	Me$_3$SiEt	Mes	30	98	96 (94)
26	4-MeC$_6$H$_4$	(structure: MeO–C$_6$H$_4$–C(O)–O–CH–CH=CH$_2$)	Mes	24	72	91 (90)

[a]Reactions were conducted in dry CH$_3$CN (15 mL) at RT in a three-neck flask under N$_2$ with a graphite anode, a Pt basket cathode, 0.150 M RCHO, 0.165 M ROH, 0.150 M DBU, 0.015 M thiazolium salt, 0.045 M TBAB, and a constant cell potential of +0.1 V vs Ag/AgNO$_3$. Mes = 2,4,6-trimethylphenyl, DiPP = 2,6-diisopropylphenyl. [b]Reactions were monitored by ^{1}H NMR spectroscopy until ester production had ceased. [c]Faradaic efficiencies assuming two-electron oxidations. [d]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard (averages of two runs); isolated yields are shown in parentheses. [e]Reaction conducted at 45 °C.

oxidation of the NHC catalyst. Reducing the voltage (1.5 V AA cell; entry 2) gave the desired ester in 22% yield. Increasing the

Table 2. NHC-Catalyzed Anodic Oxidation of Aldehydes Using Batteries as a Voltage Source[a]

entry	battery arrangement	time (h)[b]	yield (%)[c]
1	1 × 6 V, lantern battery	24	0
2	1 × 1.5 V, AA cell	48	22
3	2 × 1.5 V, AA cell (parallel)	24	31
4	4 × 1.5 V, AA cell (parallel)	36	32
5	1 × 1.5 V, D cell	24	50
6	2 × 1.5 V, D cell (parallel)	48	56
7	1 × 1.2 V, rechargeable NiCd	26	67

[a]Reactions were conducted at RT in a cylindrical vial under N$_2$ with 0.045 M TBAB, 0.150 M aldehyde, 0.165 M ROH, 0.150 M DBU, and 0.015 M 4-methyl-3-(2,4,6-trimethylphenyl)thiazolium tetrafluoroborate in CH$_3$CN. [b]Reactions were monitored by ^{1}H NMR spectroscopy until ester production had ceased. [c]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

current while maintaining the voltage by assembling multiple batteries in parallel and using D-cell batteries led to improved reaction efficiencies (entries 3−6), although ester production remained modest. Switching to a 1.2 V NiCd battery (entry 7) resulted in a more promising 67% yield after 26 h.

To achieve the necessary controlled potential, we assembled a simple voltage divider (Figure 3) consisting of a 10 Ω resistor
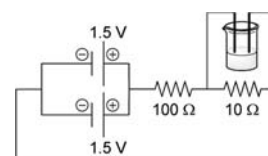

Figure 3. Circuit diagram for the organocatalyzed anodic aldehyde oxidation using a voltage divider and batteries.

in parallel with the reaction cell, which together were in series with a 100 Ω resistor. Two 1.5 V D-cell batteries were arranged in parallel as the voltage source. This setup gave a measured voltage of +0.14 V across the cell during the experiment and furnished benzyl toluate in 78% isolated yield after 27 h at room temperature (RT) and 85% isolated yield after 27 h at 45 °C. Similar success at 45 °C was achieved for 4-chlorobenzaldehyde (40 h, 90% yield), cinnamaldehyde (20 h, 94% yield), 4-methoxycinnamaldehyde (40 h, 93% yield), and nicotinaldehyde (6 h, 58% yield).

In summary, we have demonstrated the organocatalyzed anodic oxidation of aldehydes at low controlled potentials. This process involves the formation of electroactive intermediates that can be viewed as catalytically generated electroauxiliaries. Application of this approach provides a direct conversion of aldehydes to esters that circumvents the need for stoichiometric exogenous oxidants, high potentials, or redox mediators and produces minimal byproducts. This ester formation reaction is successful for a broad range of aldehyde and alcohol coupling partners. Additionally, we have shown that the process is successful using simplified electrochemical equipment such as alkaline batteries, resistors, and graphite sticks in place of potentiostats and more expensive electrodes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Detailed experimental procedures, representative cyclic voltammograms and current−time plots, and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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