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Electrochemical Minisci-type trifluoromethylation of electron-deficient heterocycles mediated by bromide ions†

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An electrochemical methodology for the Minisci-type trifluoromethylation of electron-deficient heterocycles mediated by cheap and easily available bromide ions has been developed. By virtue of the *in situ* generated sulfonyl hypobromite intermediate, the CF_3 radical can be regulated and controlled at a low concentration, thereby improving the reaction efficiency over direct electrolysis. Also, this indirect electrochemical process is performed in a beaker-type undivided cell under galvanostatic conditions, without using external expensive supporting electrolytes. This protocol provides an alternative electrochemical trifluoromethylation methodology for the late-stage functionalization of biologically important molecules.

Introduction

Trifluoromethylation reactions have attracted increasing attention in pharmaceutic, agrochemical and materials sciences since the incorporation of a CF_3 group into organic molecules can dramatically alter the physical, chemical and biological properties of the mother molecules in lipophilicity, acidity, dipole moment, metabolic stability or bioavailability.[1] As a result, various trifluoromethylation strategies have been developed, among which the radical trifluoromethylation initiated by redox chemical reagents or photocatalysts has been proved to be the main and powerful means.[2,3] Nevertheless, stoichiometric amounts of chemical redox oxidants or expensive Ir- or Ru-based photoredox catalysts are needed in most cases. Therefore, cheap and sustainable strategies for the trifluoromethylation of organic molecules are highly desirable.

Electrochemical organic synthesis, making use of electrons instead of chemical redox reagents, thereby provides an atom economical, sustainable and versatile tool for organic chemists.[4] To this end, an electrogenerated CF_3 radical has been widely used for the trifluoromethylation of organic compounds, mainly in the difunctionalization of alkenes. For example, Lin reported electrocatalytic chlorotrifluoromethylation of alkenes using Mn(II) as a mediator.[5] Later on, Lei[6] and Xu[7] independently reported the aminotrifluoromethylation and oxytrifluoromethylation of alkenes. Moreover, the electrochemical synthesis of functionalized oxindoles initiated from the anodically generated CF_3 radical followed by intramolecular radical addition with arenes was achieved by Mo,[8] Ackermann[9] and our group.[10] More recently, Wang *et al.* also described an electrochemical fluoroalkylation-migration reaction of unactivated olefins to afford fluorinated (hetero)aryl ketones.[11] On the other hand, the CF_3 radical generated from cathodic reduction of Togni's reagent could also undergo intramolecular addition with the isonitrile group to give phenanthridines.[12] Mechanically, this chemistry starts from the addition of the electrochemically generated CF_3 radical (from anodic oxidation or cathodic reduction of the CF_3 radical precursor) to the C=C bonds to give a new carbon-centered radical, which then undergoes three types of conversions, including radical coupling with other radicals, further oxidation followed by coupling with a nucleophile or radical addition to intramolecular arenes (Scheme 1a).

Compared with trifluoromethylation of alkenes, the Minisci-type electrochemical trifluoromethylation of electron-deficient heterocycles is less studied.[13] As far as we know, there is only one example on this case.[14] In 2014, Baran, Blackmond, and co-workers reported an elegant synthesis of trifluoromethylated heterocyclic pharmacophores (Scheme 1b). The electrochemical variant improved the efficiency and enhanced the yields for 20 out of 24 examples over a conventional TBHP oxidant. The improvement is supposed to result from the controlling of the CF_3 radical to a low concentration. Notably, complicated divided cells, along with an expensive Et_4NClO_4/DMSO supporting electrolyte, were required to give acceptable yields.

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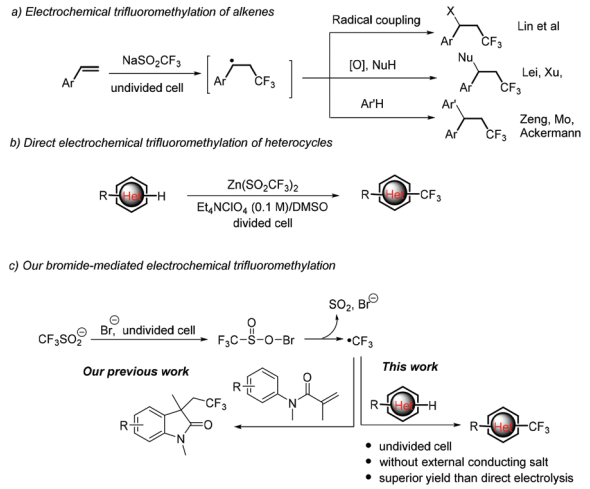


Scheme 1 Electrochemical trifluoromethylation of organic molecules.

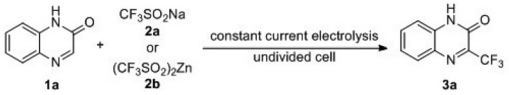
We are interested in the halide-mediated anodic oxidation for the C–H bond functionalization through ion or radical pathways.[10] More recently, we reported the electrochemical trifluoromethylation/cyclization of *N*-arylacrylamides (Scheme 1c, left).[10d] In the reaction, the initially generated trifluoromethylsulfinyl hypohalite is proposed to undergo cathodic reduction to give the corresponding sulfonyl radical, followed by evolution of SO_2 to give the CF_3 radical. In this way, the formation and concentration of the CF_3 radical can be well-manipulated and tuned, therefore providing an alternative means to address the challenge of controlling CF_3 radical concentration. Inspired by the advantage described above, we envisioned that the Minisci-type electrochemical trifluoromethylation of electrondeficient heterocycles may also achieve using bromide as the redox mediator to initiate generating the CF_3 radical (Scheme 1c, right). The realization of this hypothesis is the subject of the present communication. It is worth noting that this bromide-mediated electrochemical trifluoromethylation of heterocycles can be conducted in a simple beaker-type undivided cell employing cheap and easily available bromide ions as the redox mediator without utilization of an external large amount of supporting electrolytes. Moreover, randomly selected examples prove that this mediated electrolysis is superior to the direct electrolysis process.

Results and discussion

We commenced our studies by using quinoxaline-2(1*H*)-ones, **1a**, and more readily available sodium trifluoromethylsulfite, **2a**, as the model substrates to optimize the reaction conditions. As shown in Table 1, the desired product **3a** was obtained in 12% yield when the reaction of **1a** with **2a** was carried out in an undivided cell equipped with a platinum net as the anode and a graphite plate as the cathode at a constant current of 5 mA cm^{-2} with NaBr (1.0 equiv.) as the mediator and CH_3CN as the solvent at 50 °C. Consequent solvent screening proved that CH_3CN was preferable for the electrochemical trifluoromethylation reaction of **1a** (entries 2–5). When Baran's reagent, $Zn(CF_3SO_2)_2$ (**2b**) was employed as the CF_3 radical precursor, the yield of **3a** increased to 24% (entry 6). The evaluation of the supporting electrolyte disclosed that Et_4NBF_4 was superior and the desired product **3a** could be obtained in 33% yield (entries 7–11). In addition, Et_4NBr was demonstrated to be the best redox catalyst among the redox mediators screened and 37% yield of **3a** was afforded (entries 12–15). Notably, when the electrochemical trifluoromethylation of **1a** with **2b** was performed in the absence of a bromide redox mediator, only 21% yield of **3a** was isolated, which indicates that bromide ions play an important role in the electrochemical trifluoromethylation reaction. To our delight, the desired product **3a** could also be isolated in 40% yield in the absence of an external supporting electrolyte (entry 16); therefore the utilization of conducting salt, which generally is regarded as waste in the workup process, could be avertable. The yield of **3a** decreased successively when the loading amount of Et_4NBr was reduced (entries 17–19). Based on these results described above, we concluded that the electrochemical trifluoromethylation of quinoxaline-2(1*H*)-ones prefers the use of Et_4NBr in CH_3CN as the redox mediator and conducting salt, carried out in an undivided cell under constant current electrolysis.

With the optimal reaction conditions in hand, we turned to examine the scope and generality of the protocol by examining the reactions of various heterocycles **1** with **2b**. As shown in Table 2, the electrochemical trifluoromethylation of quinoxali-

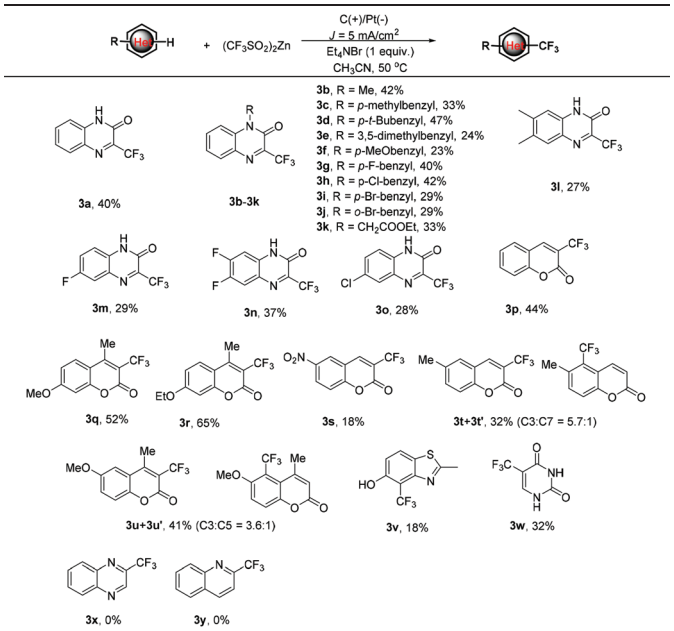
Table 1 Optimization of reaction conditions[a]



Entry	Solvent	Electrolyte (0.1 M)	Additive (equiv.)	Yield[b] (%)
1[c]	CH_3CN	$LiClO_4$	NaBr (1.0)	12
2[c]	DMSO	$LiClO_4$	NaBr (1.0)	Trace
3[c]	DMF	$LiClO_4$	NaBr (1.0)	Trace
4[c]	CH_3OH	$LiClO_4$	NaBr (1.0)	n.r.
5[c]	CH_3CN : DCE (5 : 1)	$LiClO_4$	NaBr (1.0)	11
6	CH_3CN	$LiClO_4$	NaBr (1.0)	24
7	CH_3CN	Et_4NClO_4	NaBr (1.0)	19
8	CH_3CN	Et_4NBF_4	NaBr (1.0)	33
9	CH_3CN	Bu_4NBF_4	NaBr (1.0)	28
10	CH_3CN	Bu_4NPF_6	NaBr (1.0)	23
11	CH_3CN	Bu_4NClO_4	NaBr (1.0)	18
12	CH_3CN	Et_4NBF_4	NH_4Br (1.0)	27
13	CH_3CN	Et_4NBF_4	KBr (1.0)	31
14	CH_3CN	Et_4NBF_4	Et_4NBr (1.0)	37
15	CH_3CN	Et_4NBF_4	Bu_4NBr (1.0)	34
16	CH_3CN	Et_4NBF_4	—	21
17	CH_3CN	—	Et_4NBr (1.0)	40
18	CH_3CN	—	Et_4NBr (0.5)	31
19	CH_3CN	—	Et_4NBr (0.2)	27

[a] Reaction conditions: **1a** (0.3 mmol) and **2b** (0.6 mmol) in 3 mL of solvent, undivided cell, 50 °C, current density of 5 mA cm^{-2}, graphite plate anode and Pt net cathode (working area: 1 cm^2). [b] Isolated yields. [c] CF_3SO_2Na as the CF_3 radical precursor.

Table 2 Substrate scope[a,b]



[a] Reaction conditions: **1** (0.3 mmol), **2b** (0.6 mmol), Et_4NBr (1 equiv.) in 3 mL CH_3CN, current density of 5 mA cm^{-2}, graphite plate anode and platinum net cathode (working area: 1 cm^2), undivided cell, 40 °C, 5–8 h. [b] Isolated yields.

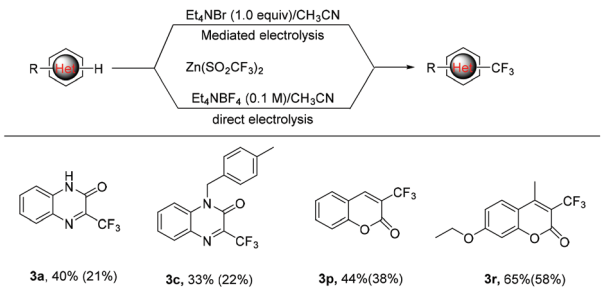
none derivatives proceeded smoothly under the standard conditions to give the corresponding 3-trifluoromethylated quinoxalinones **3b–3o** in acceptable yields. For example, when *N*-methyl-(**1b**), *N*-benzyl-(**1c–1j**) and *N*-acetate-(**1k**) substituted quinoxalinones were subjected to the electrocatalytic trifluoromethylation reaction with **2b** under the standard conditions, the corresponding products **3b–3k** were afforded in 23–47% yields. In the cases of quinoxalinones **1l–1o**, in which the substituents were on the aryl ring, the reactions also worked well to give corresponding **3l–3o**.

Other heterocyclic pharmacophores, such as coumarins, thiazole and pyrimidine, were also amenable to the protocol. For coumarin (**1p**), the corresponding **3p** was isolated in 44% yield. It was observed that the electronic characters of the substituents on the coumarin skeleton dramatically influence the reaction efficiency. For example, when electron-donating methoxy or ethoxy substituted coumarins were subjected to the reaction, the corresponding **3q** and **3r** could be obtained in 52% and 65% yields. Conversely, the substitution of an electron-withdrawing nitro group, such as **1s**, resulted in a very low yield (18%) of **3s**. Notably, when 6-methyl coumarin was subjected to the trifluoromethylation reaction with **2b**, a mixture of regioisomers **3t** and **3t′** at a ratio of 5.7 : 1 was afforded in a 32% total yield. A similar case also occurred for 6-methoxy coumarin, **1u**, wherein the mixture of regioisomers **3u**/**3u′** was isolated in 41% total yield and 3.6 : 1 ratio. The reaction also tolerated thiazole derivatives with a free hydroxyl group. For example, benzo[*d*]thiazol-5-ol, **1v**, gave corresponding **3v**, although in a bit lower yield. Finally, widely applied pharmaceutical and agrochemical, 5-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione **3w** was also afforded in 32% yield under the standard conditions.[15] However, when quinoxaline and quinoline were reacted under the standard conditions, the desired products **3x** and **3y** were not detected and the starting materials **1x** and **1y** were recovered completely.

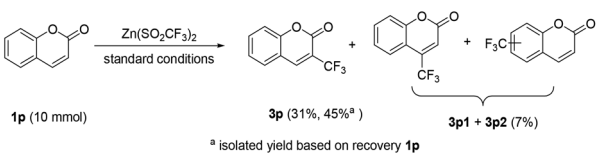
As mentioned above, the bromide-mediated trifluoromethylation reaction of **1a** with **2b** was found to be more efficient than that under direct electrolytic conditions (Scheme 2, 21% *vs.* 40%). To demonstrate the generality of this observation, we randomly selected several substrates and subjected them to electrolysis with **2b** under the standard conditions and the results are listed in Scheme 2. In accordance with what we expected, the bromide-mediated trifluoromethylation of **1c**, **1p** and **1r** gave slightly superior yields compared with that in the absence of Et_4NBr. Considering that we use undivided cells without an external expensive supporting electrolyte, the bromide-mediated trifluoromethylation protocol should be more promising for potential industrial application.

To demonstrate the practicability of the protocol, a preparative scale electrolysis was also conducted. As shown in Scheme 3, when 10 mmol of **1p** was subjected to electrolysis with **2b** under the standard conditions, the corresponding **3p** was isolated in 31% yield (45% yield based on the recovered **1p**), along with a mixture of regioisomers of **3p1** and **3p2** in 7% yield.[16]

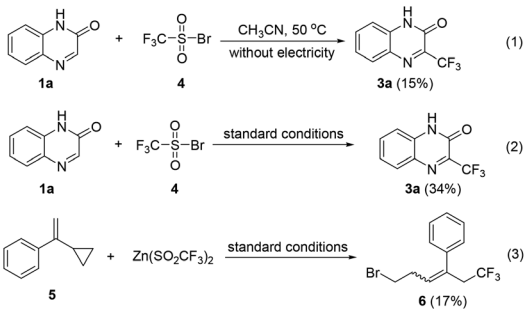
To understand the mechanism for the bromide-mediated trifluoromethylation reaction of heterocycles, a series of control experiments and cyclic voltammetric analysis were performed. As shown in Scheme 4, when the reaction of **1a** with independently synthesized trifluoro-methanesulfonyl bromide, **4**, was performed in the absence and presence of electricity, the corresponding **3a** was afforded in 15% and 34% yields, respectively. These results indicate that compound **4** could be



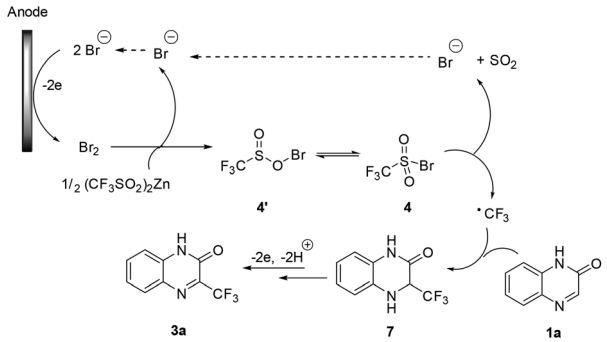
Scheme 2 Comparison of electrochemical trifluoromethylation reactions under bromide-mediated indirect and direct electrolysis (the yield in parentheses).



Scheme 3 Scale up experiment.



Scheme 4 Control experiments.



Scheme 5 A proposed Mechanism for the trifluoromethylation of quinoxalinone.

the key intermediate, and passing charge is very important. In addition, the reaction of 1-(1-cyclopropylvinyl)benzene, **5**, with **2b** gives compound **6** in 17% yield (see the ESI† for details); this radical clock experiment demonstrates that the CF_3 radical might be involved.

Cyclic voltammetric analysis was also performed to understand the possible mechanism. As shown in Fig. 1, quinoxalinone **1a** is not oxidized up to 1.30 V (curve b), whereas $Zn(CF_3SO_2)_2$ was found to be oxidized at 1.14 V (*vs.* $Ag/AgNO_3$) (curve c). Et_4NBr gave two obvious oxidation peaks at 0.49 V and 0.73 V (*vs.* $Ag/AgNO_3$) and two reduction peaks at 0.3 V and 0.62 V *vs.* $Ag/AgNO_3$ (curve d). The oxidation potential of $Zn(CF_3SO_2)_2$ is higher than that of bromide ions (1.14 V *vs.* 0.49 V and 0.73 V); therefore, the bromide ion is easier to oxidize at the surface of the anode. The CV of Et_4NBr exhibited an obvious catalytic current in the presence of **2b**, along with a new reduction peak at about 0.14 V (being the reduction of CF_3SO_2Br[10d]) *vs.* $Ag/AgNO_3$ (Fig. 1, curve e). This electrochemical behavior is quite different from that wherein the bromide ion mediates the C–H bond functionalization *via* an ionic pathway.[10h–j] This observation suggests that bromine-based active species, generated from the anodic oxidation of bromide ions, reacts with CF_3SO_2Na to afford intermediate CF_3SO_2Br, which could be reduced at the surface of the cathode.

Based on the above experiments and literature reports,[10d,14] we proposed a mechanism for the electrochemical trifluoromethylation of heterocycles. As shown in Scheme 5, anodic oxidation of bromide gives molecular Br_2, which then reacts with $Zn(CF_3SO_2)_2$ to give sulfonyl hypobromite **4′** or sulfonyl bromide **4**. Then, a cathodic reduction or a homolytic cleavage of the sulfonyl bromide **4**, followed by rapid extrusion of a SO_2 molecule, affords the key CF_3 radical. Its Minisci-type radical addition to quinoxalinone **1a** gives adduct **7**, which undergoes further anodic oxidation to afford the desired product **3a** after losing a proton.

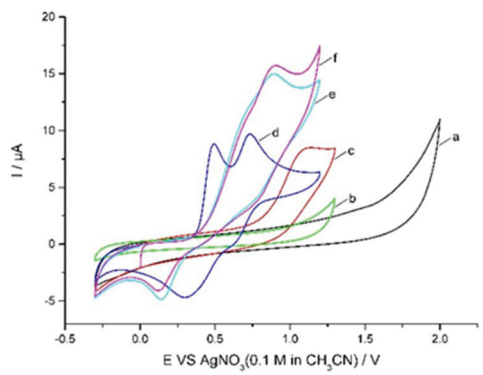


Fig. 1 Cyclic voltammograms of Et_4NBr and related compounds in 0.1 M $LiClO_4/CH_3CN$ using a glass carbon working electrode, Pt wire, and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at 100 mV s^{-1} scan rate. (a) Background, (b) **1a** (1.0 mmol L^{-1}), (c) $Zn(CF_3SO_2)_2$ (1.0 mmol L^{-1}), (d) Et_4NBr (1.0 mmol L^{-1}), (e) Et_4NBr (1.0 mmol L^{-1}) and $Zn(CF_3SO_2)_2$ (2.0 mmol L^{-1}), (f) Et_4NBr (1.0 mmol L^{-1}), $Zn(CF_3SO_2)_2$ (2.0 mmol L^{-1}) and **1a** (3.0 mmol L^{-1}).

Conclusion

In summary, electrocatalyzed Minisci-type trifluoromethylation of electron-deficient heterocycles has been developed using cheap and easily available bromide ions as the redox mediator. The method efficiently controls the concentration of the CF_3 radical by virtue of the *in situ* generated sulfonyl hypobromite as the potential CF_3 precursor. The advantage of the protocol features performing it in the simple beaker-type undivided cell, without using a large amount of external supporting electrolyte, as well as achieving superior yields to that from direct electrolysis processes, therefore providing an alternative electrochemical trifluoromethylation methodology for the late-stage functionalization of biologically important molecules.

Conflicts of interest

There are no conflicts to declare.

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