Electrochemical Nitration with Nitrite

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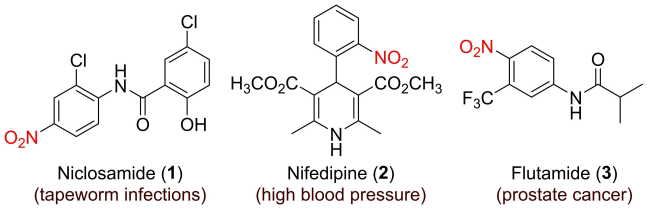
Aromatic nitration has tremendous importance in organic chemistry as nitroaromatic compounds serve as versatile building blocks. This study represents the electrochemical aromatic nitration with NBu_4NO_2, which serves a dual role as supporting electrolyte and as a safe, readily available, and easy-to-handle nitro source. Stoichiometric amounts of 1,1,1-3,3,3-hexafluoroisopropan-2-ol (HFIP) in MeCN significantly increase the yield by solvent control. The reaction mechanism is based on electrochemical oxidation of nitrite to NO_2, which initiates the nitration reaction in a divided electrolysis cell with inexpensive graphite electrodes. Overall, the reaction is demonstrated for 20 examples with yields of up to 88%. Scalability is demonstrated by a 13-fold scale-up.

Nitroaromatic compounds are among the most important functional groups in industrial chemicals and organic synthesis. Originally, mostly applied for explosives and precursor for dyes, these functions serve as excellent building blocks/key intermediates for the synthesis of drugs, agrochemicals, perfumes, and plastics due to their simple preparation combined with the facile conversion into other important moieties (such as the reduction to anilines).[1] 4-Nitrophenol for instance serves as precursor for the synthesis of the analgesic Paracetamol/Acetaminophen; one of the most consumed drugs worldwide.[2] Interestingly, nitroarenes rarely occur in nature.[1b] However, there are numerous nitro-containing approved drugs (Scheme 1), such as Niclosamide (**1**), which treats tapeworm infections.[3] The calcium channel blocker Nifedipine (**2**) is mainly used to medicate high blood pressure[3c,4] and Flutamide (**3**) is utilized against prostate cancer.[3a,c,5]

Electro-organic synthesis, a 21st century technique, offers numerous advantages in comparison to classical chemistry.[6] The substitution of hazardous chemical redox reagents by inexpensive[7] and "green" electricity,[8] derived from renewable energy sources,[9] significantly increases the atom economy and lowers the waste generation of the desired reaction.[10] Furthermore, organic electrosynthesis enables highly innovative

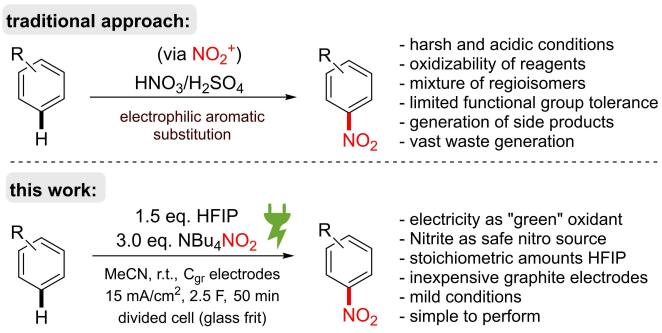


Scheme 1. Selected approved drugs containing nitro functionalities.

reactivities,[11] which imply the short-cut of synthetic steps in the preparation of value-added compounds.[12] Excellent scalability and increased on-the-job safety are further assets of this technique.[13]

Traditionally, nitroaromatic compounds are prepared by electrophilic aromatic substitution (Scheme 2). A mixture of concentrated nitric acid and sulfuric acid generates the nitronium ion (NO_2^+). Even though it is probably one of the best studied reactions and usually the method of choice for nitration, there are certain drawbacks such as the harsh and acidic reaction conditions, which often results in a mixture of regioisomers. The oxidizing power of the acidic mixture often leads to the generation of various side products due to the limited functional group tolerance. Furthermore, vast amounts of waste are generated due to the excess of mineral acids used.[1a,b,d,f,14] It is worth mentioning that the process of electrophilic aromatic nitration is hazardous and has led to a number of accidents in the past.[15] In future, nitric acid in higher concentration will be limited available in order to fulfil the homeland security aspects.[16]

Owing to the fundamental importance of nitroaromatic compounds in organic chemistry, numerous alternative ap-



Scheme 2. Traditional approach (electrophilic aromatic substitution) in comparison to the electrochemical nitration with nitrite (this work); C_{gr} = graphite.

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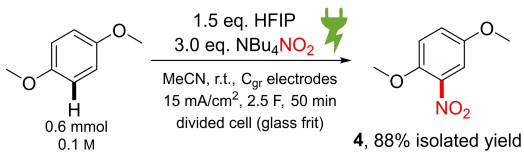
proaches have been reported in the recent decades.[14,17] Significant progress has been achieved in the field of *ipso*-nitration[18] allowing the target-oriented installation of a nitro group onto the arene. Further noteworthy advances are the use of *N*-nitrosaccharin as mild nitrating agent.[18l,19] In 2018, a photochemical methodology has been reported for the nitration of *tert*-butyloxycarbonyl (Boc)-protected anilines.[20] The electrochemical nitration, however, has not been investigated extensively so far, which motivated us to further study this possibility. An electrochemical *N*-nitration[21] and *N*-nitrosation[21,22] of secondary amines have been recently published and the electrochemical nitration of naphthalene[23] and of electron-rich catechols[24] have been studied in the past decades. In 2015, An electrochemical approach to the synthesis of nitroacetaminophen derivatives with nitrite has been reported, which is based on the direct anodic oxidation of the substrate.[25]

In this work, the electrochemical nitration of arenes, phenols and protected anilines has been accomplished by direct anodic oxidation of nitrite to NO_2/N_2O_4 in presence of stoichiometric amounts of HFIP, followed by ionic dissociation to $[NO^+][NO_3^-]$ initiating the nitration reaction. NBu_4NO_2, a highly soluble salt in organic solvents, serves as safe and easy to handle nitro source and is commercially available or can be accessed readily by salt metathesis[26] from inexpensive starting materials.



Scheme 3. Test reaction of 1,4-dimethoxybenzene with optimized reaction conditions (compare Table 1, entry 9).

Table 1. Optimization of the test reaction (Scheme 3).

Entry	Deviation from the standard conditions[a]	Yield [%][b]
1	7 mA cm^{-2}, CH_2Cl_2 instead of MeCN	69
2	7 mA cm^{-2} instead of 15 mA cm^{-2}	96(88)[c]
3	7 mA cm^{-2}, no HFIP in both compartments	31
4	7 mA cm^{-2}, no HFIP in anodic compartment	81
5	7 mA cm^{-2}, EtOH instead of HFIP (only in cathodic compartment)	14
6	7 mA cm^{-2}, glassy carbon electrodes	85
7	7 mA cm^{-2}, Pt electrodes	67
8	7 mA cm^{-2}, BDD electrodes	80
9	**none**	**96(88)**[c]
10	Ar atmosphere in anodic compartment	65
11	2.0 F instead of 2.5 F	74
12	3.5 F instead of 2.5 F	23
13	50 °C instead of RT	66
14	5 °C instead of RT	79
15	no electricity	0
16	undivided cell	0

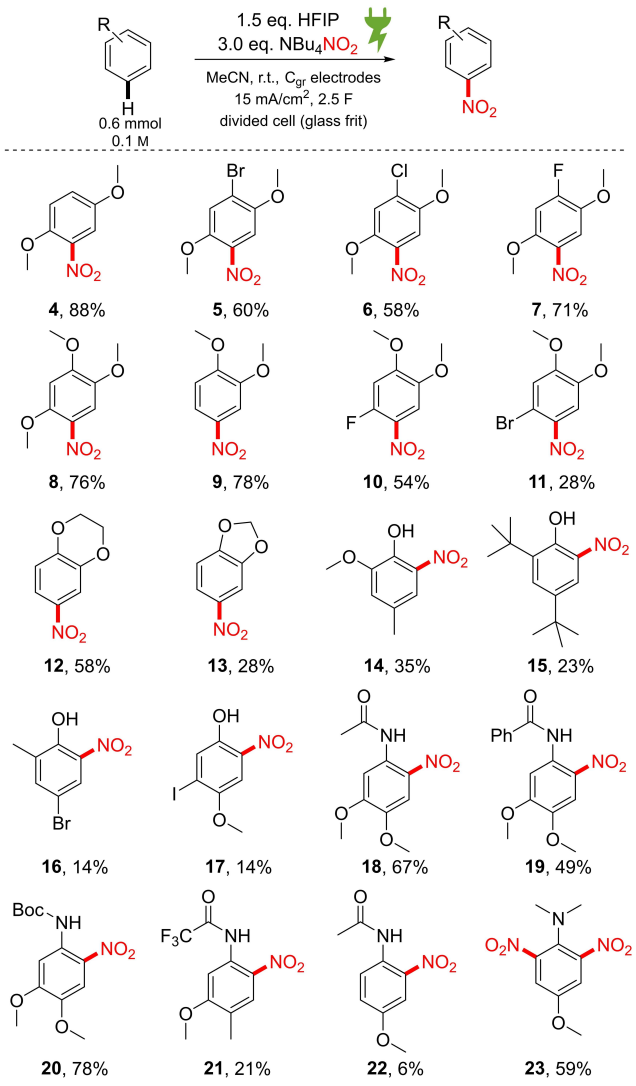
[a] Standard conditions: divided cell (glass frit), RT, time of electrolysis: 50 min, C_{gr} electrodes, $j = 15$ mA cm^{-2}, $Q = 2.5$ *F*; composition of anolyte: 1,4-dimethoxybenzene (0.6 mmol, 0.1 M), NBu_4NO_2 (3.0 equiv.), HFIP (1.5 equiv.), MeCN (5.5 mL); composition of catholyte: NBu_4BF_4 (2.0 equiv.), HFIP (0.5 mL), MeCN (5.5 mL); [b] Yield of **4** determined by internal NMR standard (1,3,5-trimethoxybenzene); [c] in brackets: isolated yield; BDD = boron-doped diamond.[27]

We began our investigations by optimizing the test reaction (Scheme 3 and Table 1). Dichloromethane as solvent provided worse results (Table 1, entry 1) in comparison to acetonitrile by giving 96% NMR yield (entry 2). Omitting of HFIP in both compartments significantly lowered the NMR yield to 31% (entry 3). However, when HFIP was only omitted in the anolyte (entry 4), the yield increased significantly, which could be explained by diffusion of low amounts of HFIP from the catholyte to the anolyte through the glass frit. Interestingly, when HFIP was substituted in the catholyte by EtOH (entry 5), the NMR yield was significantly lowered to only 14% possibly due to potential nitration or nitrosation of EtOH after diffusion to the anolyte. The investigation of different electrode materials affirmed, that graphite electrodes are superior (entry 2) in comparison to glassy carbon electrodes (entry 6), platinum electrodes (entry 7), or BDD electrodes (entry 8). To our delight, the increase of the current density (*j*) to 15 mA cm^{-2} (entry 9) provided same results in comparison to 7 mA cm^{-2} (entry 2), which led to significantly lower electrolysis durations (50 min).

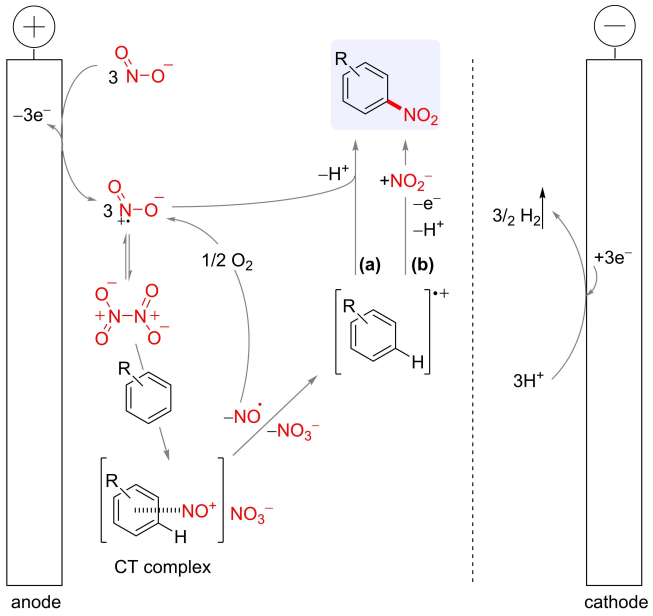
Interestingly, worse results were obtained, when the electrolysis was conducted in an Ar atmosphere in the anodic compartment (entry 10). The modulation of the applied amount of charge (*Q*) to 2.0 *F* lowered the NMR yield to 74% (entry 11), whereas 3.5 *F* led to significantly worse results (entry 12). Elevated (50 °C, entry 13) as well as lower (5 °C, entry 14) reaction temperatures resulted in depressed product formation. No electricity (entry 15) or the electrolysis in an undivided cell (entry 16) rendered in no product formation. Finally, the conditions from entry 9 were applied for further experiments and **4** was isolated in 88%. The solvent-control of anodic conversions is a modern tool in electro-organic synthesis.[28] In particular, HFIP can promote by solvation effects of the individual coupling partners unique selectivity.[29] Moreover, HFIP is prone to block oxygen moieties, whereas other heteroatoms can selectively enter the reactions scenario.[11a–c]

Thereupon, the scope of the reaction was further investigated as displayed in Scheme 4. Halogen substituents were tolerated, as **5** (60%), **6** (58%), and **7** (71%) were isolated in good to moderate yields. **8**, equipped with three methoxy substituents, was isolated in 76% and veratrole resulted in **9** (78%). 4-Fluoroveratrole gave **10** in 54%, whereas **11** derived from 4-bromoveratrole was only isolated in 28%. The nitration of 1,4-benzodioxane gave **12** in 58% and heterocyclic structure **13** provided only 28% isolated yield. Most remarkably, no further regioisomers were detected by GC and GC-MS investigation of the crude reaction mixtures, which is evidence for the exquisite selectivity of this nitration reaction. Next, we aimed to investigate the eligibility of this reaction towards several phenols, which were isolated in yields ranging 14%–35% (**14**, 35%; **15**, 23%; **16**, 14%; **17**, 14%), whereby we conclude that this approach is not fully suitable for phenolic substrates. Nevertheless, phenols can be nitrated relatively simple even with diluted nitric acid.[30]

Thereafter, we decided to explore the nitration towards aniline derivatives. Acetanilide and benzanilide derivatives were



Scheme 4. Scope of the reaction demonstrated in isolated yields.



Scheme 5. Postulated reaction mechanism for the nitration of aromatic compounds.

suitable for this methodology as **18** was isolated in 67% and **19** in 49% yield. To our delight, Boc-protected aniline **20** was obtained in 78%, which offers complementarity to the common nitration with mineral acids as these immediately cleave the Boc protection group. Trifluoroacetanilide **21** was isolated in significantly lower yields (21%). 4-Methoxyacetanilide was not suitable for this protocol (**22**, 6%). Surprisingly, *N*,*N*-dimethyl-4-methoxyaniline resulted in the double nitrated product **23** in 59% yield. This could be explained by the *N*-directing effect of the dimethylamino moiety and the electron-rich nature of the substrate.[31]

The postulated reaction mechanism is displayed in Scheme 5. Cyclic voltammetry confirms the initial anodic oxidation of nitrite to NO_2, which is in equilibrium to N_2O_4. It is noteworthy that the addition of HFIP slightly increases the oxidation potential of nitrite by hydrogen bonding effects (see the Supporting Information). The formation of [Arene–NO^+] charge-transfer complexes[32] upon ionic dissociation of N_2O_4 to [NO^+][NO_3^-] is well described in literature.[33] The ionic dissociation of N_2O_4 is considered to be favored under polar conditions,[34] which could explain the positive effect of acetonitrile as solvent and stoichiometric amounts of HFIP in this reaction. The nitrosonium ion acts as oxidant leading to the generation of arene radical cations combined with NO generation.[35] The latter could be partially recycled to the system forming NO_2 by oxidation with atmospheric oxygen[35a] as depicted in Scheme 5. This rationalizes the worse results obtained in Ar atmosphere (Table 1, entry 10). The in-situ generated arene radical cation could then either react with another equivalent of NO_2 (a)[33,35a] in combination with H^+ abstraction to form the desired aromatic nitro compound. Path b suggests that NO_2^- could undergo nucleophilic attack to the arene radical cation, followed by a second oxidation step with H^+ abstraction. Further explanations for the positive effect of HFIP could be the stabilization of the arene radical cation[36] or the [arene–NO^+] complex analogously to the stabilization of the [arene–NO_2^+] π-complex by HFIP as reported from Hua and coworkers.[17i] As cathodic side reaction, H_2 gas formation has been observed.

In fact, the nitration of aromatic compounds as well as the nitration of alcohols and amines with NO_2/N_2O_4 has been investigated in the past decades.[23a,33,34,37] However, this approach seems dangerous and not very practical due to the toxic and gaseous nature of nitrous gases. In this work, the anodic oxidation of nitrite to NO_2 elegantly circumvents these drawbacks and allows reaction control.

Finally, a 13-fold scale-up reaction in a H-type divided cell (glass frit) was conducted in order to investigate the scalability of the reaction (Figure 1). Nitroarene **4** was obtained in 85% isolated yield (1.25 g), which is in the same range compared to the normal scale as shown in Scheme 4 (88%). It is noteworthy that the anolyte turned red during electrolysis and gas

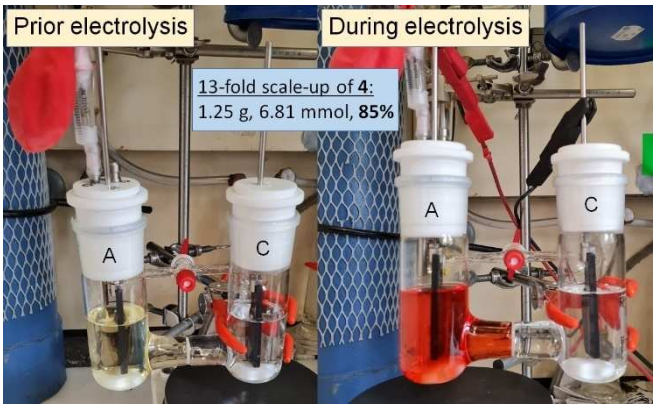


Figure 1. 13-Fold scale-up reaction of **4** in a H-type divided cell with a glass frit; left: cell setup prior electrolysis; right: cell setup during electrolysis (after passing ca. 1 F); A = anodic compartment; C = cathodic compartment.

evolution (NO gas) was observed in the anodic compartment. These observations support the postulated mechanism shown in Scheme 5. The red color could arise from the formation of NO_2 and/or the color of the [arene–NO^+] charge transfer complexes, which are described as yellow to red in prior reports.[32,33]

In summary we have developed the first electrochemical nitration of arenes, phenols, and aniline derivatives with NBu_4NO_2 as a supporting electrolyte and safe, readily available, and easy-to-handle nitro source. Inexpensive electricity serves as the "green" and inexpensive oxidant. Stoichiometric amounts of HFIP significantly improve the yield of this reaction. The selectivity and conversion are promoted by the action of hydrogen bonding. The reaction mechanism proceeds via direct anodic oxidation of nitrite to NO_2. The formation of [arene–NO^+] charge-transfer complexes is supposed to induce the oxidation of the electron-rich arene to form the arene radical cation, which recombines with NO_2 or nitrite to yield the nitroaromatic compound. Overall, 20 examples have been demonstrated with yields up to 88%. Scalability has been demonstrated in a 13-fold scale-up reaction.

Experimental Section

The anodic compartment of a divided screening cell was charged with the aromatic compound (0.60 mmol, 1.00 equiv.) and NBu_4NO_2 (519 mg, 1.8 mmol, 3.00 equiv.). The cathodic compartment was charged with NBu_4BF_4 (395 mg, 1.2 mmol, 2.00 equiv.), MeCN (5.5 mL), and HFIP (0.5 mL). Into the anodic compartment were added MeCN (5.5 mL) and HFIP (94 μL, 0.90 mmol, 1.50 equiv.). The graphite electrodes were connected to a galvanostat and the electrolysis ($j = 15$ mA cm^{-2}, $Q = 2.5$ F) was carried out under stirring (300 rpm) at room temperature. During this process, the terminal voltage was ~13.5 V. After termination of the electrolysis (50 min), the reaction mixture was further stirred for 30 min. Ethyl acetate (30 mL) was added to the reaction mixture. The organic layer was washed with distilled water (3×25 mL). The aqueous phases were back-washed with ethyl acetate (2×25 mL). The combined organic fractions were dried over Na_2SO_4 and filtered. The organic solvent was removed under reduced pressure. The crude product was separated by column chromatography by using an ethyl acetate/cyclohexane solvent gradient (mostly 2:98 to 1:1).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrochemistry · green chemistry · nitrogen oxides · radicals · synthetic methods

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