Advanced Synthesis & Catalysis

Title: Electrochemical Synthesis of <i>O</i>-Phthalimide Oximes from Vinyl Azides <i>via</i> Radical Sequence: Generation, Addition and Recombination of Imide-<i>N</i>-Oxyl and Iminyl Radicals with C-O / N-O Bonds Formation

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Electrochemical Synthesis of *O*-Phthalimide Oximes from *α*-Azido Styrenes *via* Radical Sequence: Generation, Addition and Recombination of Imide-*N*-Oxyl and Iminyl Radicals with C-O / N-O Bonds Formation

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Abstract. Electrochemically induced radical-initiated reaction of vinyl azides with *N*-hydroxyphthalimide resulting *O*-phthalimide oximes with challenging for organic chemistry N-O-N fragment has been discovered. The developed approach introduces in synthesis electrochemically generated O-centered imide-*N*-oxyl radicals as the coupling components. Sequential formation of C-O and N-O bonds was achieved *via* generation and selective addition of imide-*N*-oxyl radicals, followed by recombination with iminyl radicals. A wide range of *O*-phthalimide oximes was obtained with the yields up to 84%.

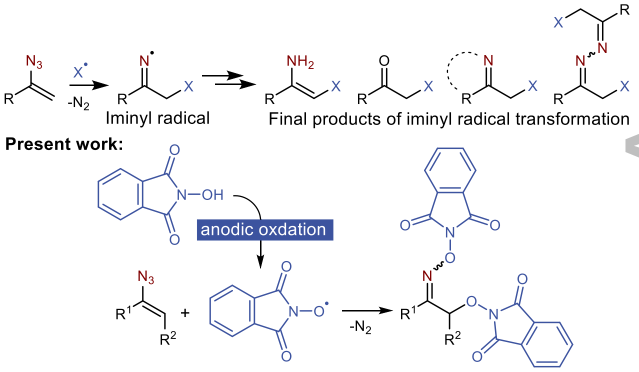
Keywords: electrosynthesis; vinyl azides; N-oxyl radicals; N-hydroxyphthalimide; *O*-phthalimide oximes; N-O bond

Introduction

Currently, electroorganic synthesis is witnessing a renaissance, being one of the most actively developing areas of modern organic chemistry.[1] Using an electrochemical methodology, a number of approaches to the synthesis of important natural compounds,[2] industrial products,[3] and heterocyclic structures[4] was created. Great attention is paid to the electrochemical C-H functionalization,[5] oxidative coupling[6] and difunctionalization of alkenes and alkynes.[7] Such processes are often accompanied by the formation of reactive radical species that play a key role in the formation of the desired structures.[8] Electric current is extensively used as a convenient tool for the direct or indirect generation of C-,[9] O-,[10] N-[11] and S-centered[12] radicals.

Electrochemical reactions involving stabilized O-centered *N*-oxyl radicals represent a challenging area of electrosynthesis.[13] Generation of imide-*N*-oxyl radicals as a result of anodic oxidation of *N*-hydroxyimides and their selective reactions with substrates remains problematic due to the low stability of such radicals under electrochemical conditions and their tendency to self-decomposition.[14] Although imide-*N*-oxyl radicals are widespread in many processes of C-O coupling[15] and functionalization of alkenes,[16] their use in electroorganic synthesis is limited to reactions in which they act as mediators of benzylic[17] and allylic[18] C-H functionalization, as well as various oxidation processes.[19]

Reactions involving vinyl azides, in which various radical species add to the terminal carbon atom of the double C=C bond of vinyl azide with the release of N_2 molecule, gain growing interest (Scheme 1).[20]



Scheme 1. Present work in the context of the radical transformations involving vinyl azides and iminyl radicals.

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As a rule, the outcome of such processes is formation of iminyl radical and its subsequent transformations resulting enamines[21] or ketones,[22] as well as intramolecular cyclization[23] or homocoupling.[24] To the best of our knowledge there are no examples of the selective intermolecular addition reactions involving iminyl radicals.

In the present work, it was found that imide-*N*-oxyl radicals, anodically generated from *N*-hydroxyphthalimide selectively react with vinyl azides resulting in the formation of *O*-substituted oximes with N-O-N fragment (hereinafter «*O*-phthalimide oximes»). The main feature of the work is the formation of a new N-O bond through the recombination of *N*-centered iminyl radicals and O-centered *N*-oxyl radicals. Surprisingly, no products of iminyl radical reduction or dimerization were observed. The stability of N-O bond in the discovered process was unforeseen due to its electrochemical lability and a tendency to cathodic reduction.[25]

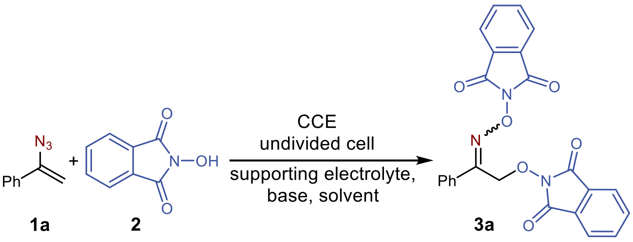
It should be noted that the products of the discovered reaction bear two fundamentally important functionalities – analogue of oxime ether and *N*-alkoxyphthalimide. Oxime ethers have attracted much attention due to their biological activities and wide variety of synthetic applications.[26] Oxime ethers exhibit fungicidal,[27] insecticidal,[27] herbicidal,[28] antibacterial,[29] anticonvulsive[30] and anticancer[31] effects. They are used in organic synthesis, providing valuable synthons to obtain a number of medicinal heterocyclic compounds.[32] Recently, oxime ethers have been extensively employed as the precursors of iminyl radicals in the various processes of radical oxidative coupling and cyclization.[33] On the other hand, *N*-alkoxyphthalimides are becoming increasingly common in various photocatalytic transformations as the precursors of O- and C-centered radicals.[34] With this in mind, the development of new methods for the synthesis both of oxime ethers and *N*-alkoxyphthalimides is an urgent task of modern organic chemistry.

Results and Discussion

One of the key points of the work is the preparative generation of stable *N*-oxyl radicals based on the direct anodic oxidation of *N*-hydroxy compounds. Unlike traditional methods for generating such radical, this approach is does not imply the use of toxic and expensive oxidants.

We commenced our investigations with the optimization of the model electrochemical reaction of (1-azidovinyl)benzene **1a** with *N*-hydroxyphthalimide **2**, resulting *O*-phthalimide oxime **3a**. The data concerning the influence of the solvent nature, type of supporting electrolyte, base and its molar ratio to *N*-hydroxyphthalimide, amount of the passed electricity and current density are summarized in Table 1. All the reactions were carried out in a thermostatically controlled undivided electrochemical cell at 15 °C in an air atmosphere.

Table 1. Optimization of *O*-phthalimide oxime **3a** electrosynthesis from vinyl azide **1a** and *N*-hydroxyphthalimide 2. [a]



№	solvent	base (molar ratio mol/mol **2**)	electrolyte	yield of **3a** (%)[b]
1	acetone	pyridine (1.5)	$LiClO_4$	n.d.
2	acetone	pyridine (1.5)	n-Bu_4NClO_4	27
3	acetone	pyridine (1.5)	n-Bu_4NBF_4	30
4	acetone	pyridine (1.5)	$[LutH]ClO_4$	62
5	acetone	pyridine (1.5)	$[LutH]BF_4$	60
6	acetone	pyridine (1.5)	$[PyH]ClO_4$	65
7	CH_3CN	pyridine (1.5)	$[PyH]ClO_4$	47
8	THF[c]	pyridine (1.5)	$[PyH]ClO_4$	50
9	DCM	pyridine (1.5)	$[PyH]ClO_4$	51
10	DMF	pyridine (1.5)	$[PyH]ClO_4$	19
11	MeOH	pyridine (1.5)	$[PyH]ClO_4$	n.d.
12	HFIP	pyridine (1.5)	$[PyH]ClO_4$	n.d.
13	acetone	2,6-lutidine (1.5)	$[PyH]ClO_4$	62
14	acetone	2,4,6-collidine (1.5)	$[PyH]ClO_4$	61
15	acetone	DBU (1.5)	$[PyH]ClO_4$	59
16	acetone	Et_3N (1.5)	$[PyH]ClO_4$	58
17	acetone	DABCO (1.5)	$[PyH]ClO_4$	28
18	acetone	DMAP (1.5)	$[PyH]ClO_4$	19
19	**acetone**	**pyridine (1.0)**	**$[PyH]ClO_4$**	**85 (83)**
20	acetone	pyridine (0.5)	$[PyH]ClO_4$	64
21	acetone	-	$[PyH]ClO_4$	35
22[d]	acetone	pyridine (1.0)	$[PyH]ClO_4$	80
23[e]	acetone	pyridine (1.0)	$[PyH]ClO_4$	82
24[f]	acetone	pyridine (1.0)	$[PyH]ClO_4$	63
25[g]	acetone	pyridine (1.0)	$[PyH]ClO_4$	n.d.
26[h]	acetone	pyridine (1.0)	$[PyH]ClO_4$	29
27[i]	acetone	pyridine (1.0)	$[PyH]ClO_4$	55

[a] Reaction conditions: **1a** (0.5 mmol, 73 mg), **2** (1.0 mmol, 163 mg), base (0.5–1.5 mmol, 40–489 mg), electrolyte (0.5 mmol, 90–171 mg), solvent (15.0 mL), undivided cell, graphite plate anode (15 × 25 × 3 mm), platinum plate cathode (15 × 25 × 0.1 mm), constant current electrolysis with i = 60 mA (j_{anode} = 16 mA/cm^2), F = 1.1 F/mol **2** (reaction time 29 min), 15 °C.

[b] Yield determined by ^{1}H NMR. Isolated yields are given in parentheses. n.d. – not detected. The bold line of entry 19 indicates the conditions as optimal.

[c] 0.5 mL of H_2O added.

[d] 1.5 F/mol **2** of electricity passed (reaction time 40 min).

[e] Constant current i = 40 mA (j_{anode} = 10.7 mA/cm^2).

[f] Constant current i = 80 mA (j_{anode} = 21.3 mA/cm^2).

[g] Without electricity.

[h] Pt plate anode (15 × 25 × 0.1 mm).

[i] Ni plate cathode (15 × 25 × 0.1 mm).

The nature of an electrolyte turned out to be the key factor influencing in the studied process (Table 1, entries 1–6). The initial experiment in acetone using pyridine as a base and $LiClO_4$ as a supporting electrolyte does not allow to obtain product **3a** (Table 1, entry 1). We speculate that the negative result was caused by the formation of an insoluble red precipitate, apparently, a salt of *N*-hydroxyphthalimide, which covered the electrodes surface and suppressed the reaction.[35] Thus, we turned our attention to organic electrolytes. Employing quaternary ammonium salts (n-Bu_4NClO_4 and n-Bu_4NBF_4), we obtained product **3a** with a yield of 27–30% (Table 1, entries 2 and 3). Based on the data concerning successful electrochemical generation of imide-*N*-oxyl radicals[17b] we decided to examine 2,6-lutidinium salts as a supporting electrolyte. To our delight, reaction with $[LutH]ClO_4$ and $[LutH]BF_4$ resulted **3a** with considerably higher yield (Table 1, entries 4 and 5, 60–62%). Further screening revealed pyridinium perchlorate ($[PyH]ClO_4$) as the best electrolyte for the process under study, providing **3a** with a 65% yield (Table 1, entry 6).

Entries 7–12 showed that acetone was an optimal solvent. When carrying out the reaction in other polar aprotic solvents such as CH_3CN, THF and DCM, the yield of product **3a** did not exceed 51% (Table 1, entries 7–9). Reaction in DMF (Table 1, entry 10) resulted **3a** with the yield of 19%. In the reactions with MeOH and HFIP the formation of **3a** was not observed (Table 1, entries 11 and 12).

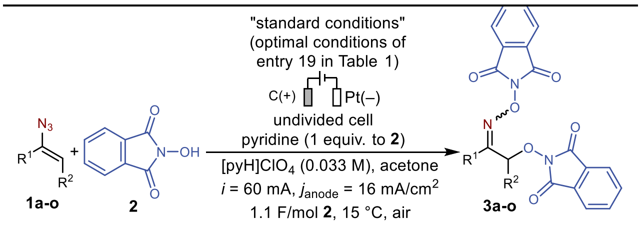
The nature of a base and its amount significantly affects the yield of target product **3a**. Pyridine-type bases, such as 2,6-lutidine and 2,4,6-collidine, as well as DBU and Et_3N showed slightly lower efficacy compared to pyridine (Table 1, entries 13–16, yield of **3a** 58–62%). DABCO and DMAP (Table 1, entries 17 and 18) turned out to be unsuitable for the process under study; in these cases, the yield of **3a** did not exceed 28%. Thus, pyridine was chosen as an optimal base, and then the influence of its amount on **3a** yield was studied. Usage equimolar amount of pyridine with respect to *N*-hydroxyphthalimide **2** caused a noticeable increase in the yield of *O*-phthalimide oxime **3a** (Table 1, entry 19, 85%), while decrease in the amount of the base to 0.5 equivalents or its absence diminished the yield of the reaction product (Table 1, entries 20 and 21, yield **3a** 35–64%).

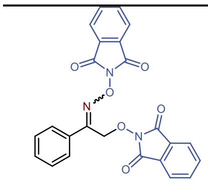
The optimal amount of electricity to carry out the reaction is 1.1 F/mol **2**; in this case, the current efficiency is 91%. Reaction with the larger amount of electricity (F = 1.5 F/mol **2**) led to a slight decrease in the yield of **3a** (Table 1, entry 22, 80%). Both increasing and decreasing the current density reduced the yield of **3a** (Table 1, entries 23 and 24, 63–82%). The target product was not obtained in the absence of electricity (Table 1, entry 25).

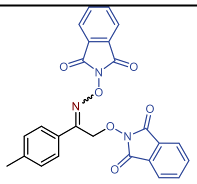
When varying the materials of the electrodes, the use of a platinum anode, as well as a nickel cathode, drastically reduced the yield of the target product (Table 1, entries 26 and 27, 29–55% yield).

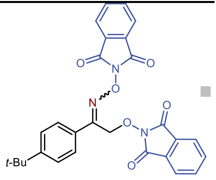
Under the optimal conditions (Table 1, entry 19), we showed the applicability of the discovered process on a variety of vinyl azides **1** (Table 2).

Table 2. Electrochemical synthesis of *O*-phthalimide oximes **3a-o** from vinyl azides **1a-o** and *N*-hydroxyphthalimide **2**.[a,b]

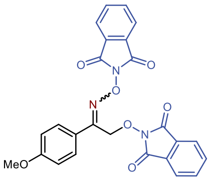



3a, 83% (0.84:1)

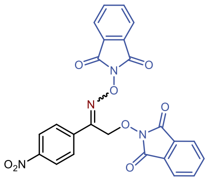

3b, 84% (0.89:1)



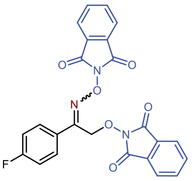
3c, 82% (0.75:1)



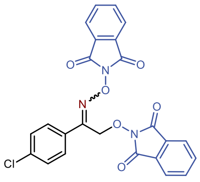
3d, 53% (0.97:1)



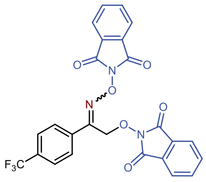
3e, 40% (0.12:1)



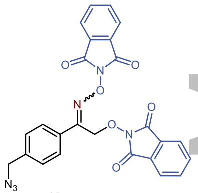
3f, 70% (0.88:1)



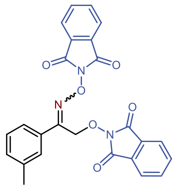
3g, 71% (0.22:1)

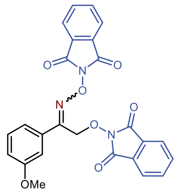


3h, 60% (0.8:1)

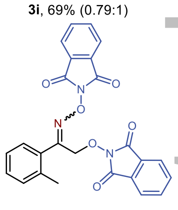


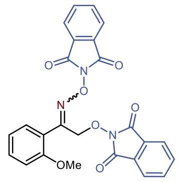
3i, 69% (0.79:1)


3j, 81% (0.88:1)

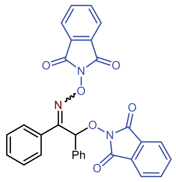


3k, 63% (0.95:1)

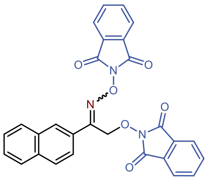

3l, 65% (0.72:1)



3m, 59% (0.86:1)



3n, 54%

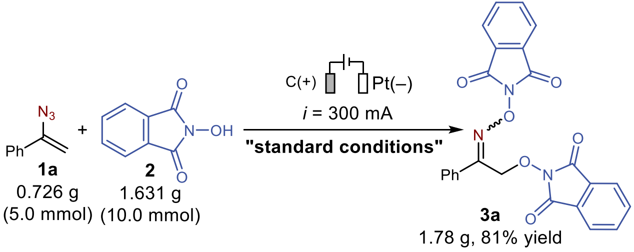

3o, 42% (0.75:1)

[a] Reaction conditions: **1a-o** (0.5 mmol, 73–111 mg), **2** (1.0 mmol, 163 mg), pyridine (1.0 mmol, 79 mg), $[pyH]ClO_4$ (0.5 mmol, 90 mg), acetone (15.0 mL), undivided cell, graphite plate anode (15 × 25 × 3 mm), platinum plate cathode (15 × 25 × 0.1 mm), constant current electrolysis with i = 60 mA (j_{anode} = 16 mA/cm^2), F = 1.1 F/mol **2**, 15 °C, air atmosphere.

[b] Isolated yield. Stereoisomeric ratios determined by ^1H NMR are given in parentheses.

The reaction successfully proceeds with various aryl-containing vinyl azides **1b-m** bearing electron-donating alkyl and methoxy-groups in para-, meta-, and ortho- positions (**3b-d**, **3i-m**, yield 53-84%) as well as electron-withdrawing (NO$_2$, halogens, CF$_3$) substituents (**3e-3h**, yield 40-70%). β-Substituted vinyl azide **1n** also enter the studied transformation, giving *O*-phthalimide oxime **3n** (yield 54%). In the reaction with 2-(1-azidovinyl)naphthalene **1o**, product **3o** was obtained with the yield of 42%.

The synthetic utility of the developed protocol was demonstrated by the synthesis of product **3a** on a gram scale amount (Scheme 2).



Scheme 2. Gram scale synthesis of *O*-phthalimide oxime **3a**.

In the reaction of 5 mmol of vinyl azide **1a** with 10 mmol of *N*-hydroxyphthalimide **2** we obtained 1.78 g of target *O*-phthalimide oxime **3a** that corresponds to the yield of 81%.

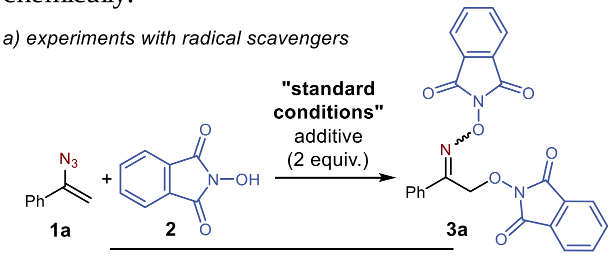
To clarify the reaction mechanism, we carried out series of experiments with radical scavengers, cyclic voltammetry and EPR analysis (Scheme 3).

Electrochemical reaction under standard conditions for the synthesis of *O*-phthalimide oximes (Table 1, entry 19) in the presence of 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO), 1,1-diphenylethylene and butylated hydroxytoluene (BHT) (Scheme 3a) led to a significant decrease in the yield of product **3a**, which indicated radical nature of the discovered process.

According to the results of the CV experiments (Scheme 3b), we conclude that vinyl azide **1a** and pyridine are electrochemically inert in the range of -0.5–1.4 V *vs.* Ag/AgNO$_3$ (curves b and c). On the voltammogram of NHPI **2** solution (curve d), we observe the weak peaks at 0.69 V and 0.58 V, corresponding to the reversible oxidation of NHPI **2** to phthalimide-*N*-oxyl radical. Addition of 1 equiv. of pyridine to the NHPI **2** solution (curve e) led to a significant increase of the oxidation and reduction currents (peaks at 0.96 V and 0.40 V, respectively).[36] In the presence of vinyl azide **1a**, the peak of reduction of phthalimide-*N*-oxyl radical disappeared (curve f), which indicated its interaction with vinyl azide.

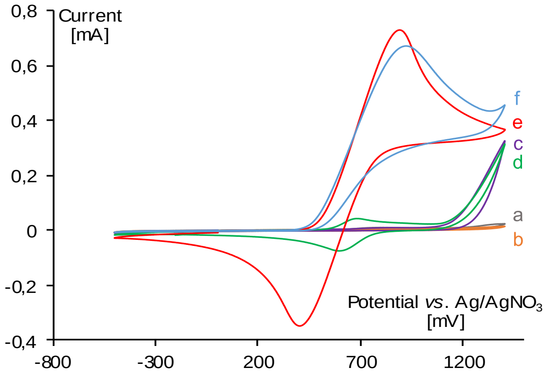
To further confirm the formation of the phthalimide-*N*-oxyl radical in the studied electrochemical system, an *in-situ* EC-EPR experiment was conducted (Scheme 3c). A solution of *N*-hydroxyphthalimide **2** and pyridine in *n*-Bu$_4$NClO$_4$/MeCN was electrolyzed inside an EPR cavity of spectrometer and EPR spectrum was recorded simultaneously. The parameters of the observed signal, such as *g*-factor and hyperfine coupling constant, are in agreement with the literature data for the phthalimide-*N*-oxyl radical generated chemically.[37]

a) experiments with radical scavengers



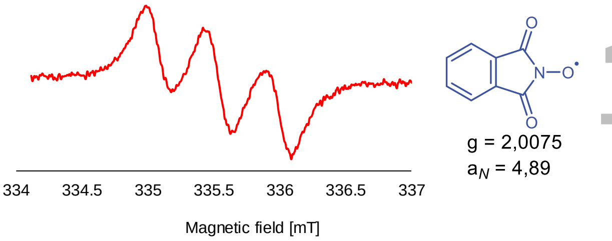
Additive	Yield of **3a** (%)
-	85
TEMPO	29
1,1-diphenylethylene	24
BHT	20

*b) CV studies of vinyl azide **1a**, N-hydroxyphthalimide **2** and pyridine*



(a) Background; (b) Pyridine (0.05 M); (c) **1a** (0.025 M); (d) **2** (0.05 M); (e) **2** (0.05 M) and pyridine (0.05 M); (f) **1a** (0.025 M), **2** (0.05 M) and pyridine (0.05 M) in [pyH]ClO$_4$/acetone (0.1 M)

c) Electrochemical generation of phthalimide-N-oxyl radical: EPR study

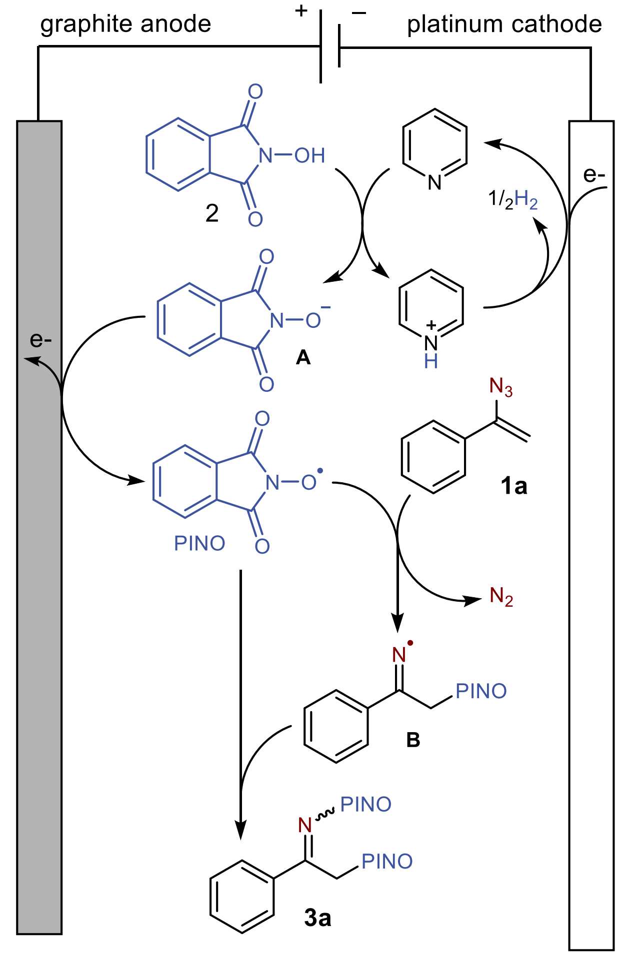


Conditions: electrolysis of NHPI/pyridine solution in *n*-Bu$_4$NBF$_4$/MeCN for 30 s, then recording a spectrum

Scheme 3. Experiments on the confirmation of the reaction mechanism.

Based on the results of the control experiments and literature data on electrochemical generation of imide-*N*-oxyl radicals from *N*-hydroxyimides and the addition of radical species to vinyl azides, we suggested the reaction mechanism of electrochemical synthesis of *O*-phthalimide oxime **3a** involving transformation of vinyl azide **1a** under the action of *N*-hydroxyphthalimide **2** (Scheme 4).

Initially, deprotonation of *N*-hydroxyphthalimide **2** under the action of pyridine gives anion **A**, the anodic oxidation of which leads to the formation of phthalimide-*N*-oxyl radical (PINO).[36, 38] Subsequently, PINO adds to the terminal carbon atom of double C=C bond of vinyl azide **1a** with the elimination of N$_2$ molecule and formation of iminyl radical **B**.[20] At the last stage recombination of **B** and PINO radicals occurs giving final product **3a**.



Scheme 4. Proposed mechanism for the electrochemical synthesis of *O*-phthalimide oxime **3a** from vinyl azide **1a** and *N*-hydroxyphthalimide **2**.

Conclusion

In conclusion, we disclosed the electrochemically induced reaction between vinyl azides and *N*-hydroxyphthalimide resulting *O*-phthalimide oximes with N-O-N fragment. The reaction is implemented in an undivided cell and produces the desired *O*-phthalimide oximes in moderate to high yields. The developed approach is applicable to a wide range of α-azido styrenes and is tolerant to various electron-withdrawing and donating groups. The radical route commences with the anodic generation of stabilized phthalimide-*N*-oxyl radicals, which coupled twice with starting vinyl azide and intermediate iminyl radical to form C-O and N-O bonds. Cyclic voltammetry and EPR spectroscopy confirmed the key role of imide-*N*-oxyl radicals in the developed process. The finding of the work is the application of pyridine as a base and pyridinium perchlorate as an electrolyte, which facilitates the anodic generation of phthalimide-*N*-oxyl radicals and simultaneously protects the N-O fragment from cathodic reduction. The synthesis is successfully scaled to obtain the target products in gram quantities. The proposed approach opens up great opportunities for the selective introduction of valuable hydroxylamine fragment into various organic molecules under electrochemical conditions.

Experimental Section

General Procedure for Optimization of *O*-Phthalimide Oxime 3a Electrosynthesis (Experimental Procedure for Table 1)

An undivided 25 mL two-neck jacketed cell was equipped with reflux condenser, graphite anode (15 × 25 × 5 mm, S = 3.75 cm^2) and a platinum plate cathode (15 × 25 × 5 mm, S = 3.75 cm^2), and connected to a DC regulated power supply. A solution of (1-azidovinyl)benzene **1a** (0.5 mmol, 145 mg), *N*-hydroxyphthalimide **2** (1.0 mmol, 163 mg), base (pyridine, 2,6-lutidine, 2,4,6-collidine, DMAP, DABCO, DBU, Et_3N or Cs_2CO_3, 0.5–1.5 mmol, 40–489 mg) and supporting electrolyte ([LutH]ClO_4, [LutH]BF_4, [PyH]ClO_4, *n*-Bu_4NClO_4 or *n*-Bu_4NBF_4, 0.5 mmol, 90–171 mg,) in 15.0 mL of solvent (DCM, CH_3CN, acetone, acetone with 0.5 mL of H_2O, MeOH, HFIP, THF with 0.5 mL of H_2O or DMF) was electrolyzed using constant current conditions (i = 60 mA, j_{anode} = 16 mA/cm^2) at 15 °C under magnetic stirring. After passing 1.1–1.5 F/mol **2** of electricity (reaction time 29–40 min), electrodes were washed with DCM (2 × 20.0 mL). The combined organic phases were concentrated under reduced pressure using a rotary evaporator (15–20 mmHg), bath temperature ca. 50-55 °C. The yield of product **3a** was determined by ^1H NMR analysis of a crude mixture using *p*-methoxyacetophenone as the internal standard. In the entry 19 product **3a** was isolated by flash column chromatography on silica gel using DCM/EtOAc mixture as eluent (with the volume part of EtOAc gradually increased from 2% to 4%).

Typical Procedure for the Electrosynthesis of the *O*-Phthalimide Oximes 3a–o (Experimental Procedure for Table 2)

An undivided 20 mL two-neck jacketed cell was equipped with reflux condenser, graphite anode (15 × 25 × 5 mm, S = 3.75 cm^2) and a platinum plate cathode (15 × 25 × 5 mm, S = 3.75 cm^2), and connected to a DC regulated power supply. A solution of vinyl azide **1a–o** (0.5 mmol, 73–114 mg), *N*-hydroxyphthalimide **2** (1.0 mmol, 163 mg), pyridine (1.0 mmol, 79 mg) and [PyH]ClO_4 (0.5 mmol, 90 mg,) in 15.0 mL of acetone was electrolyzed using constant current conditions (i = 60 mA, j_{anode} = 16 mA/cm^2) at 15 °C under magnetic stirring. After passing 1.1 F/mol of electricity (reaction time 29 min), electrodes were washed with DCM (2 × 20 mL). The combined organic phases were concentrated under reduced pressure using a rotary evaporator (15–20 mmHg), bath temperature ca. 50-55 °C. Products **3a-o** were isolated by column chromatography on silica gel using DCM/EtOAc mixture as eluent (with the volume part of EtOAc gradually increased from 2% to 4%).

Experimental Procedure for Scheme 3

Reaction of Vinyl Azide 1a with N-hydroxyphthalimide 2 in Standard Conditions in the Presence of Radical Scavengers

An undivided 25 mL two-neck jacketed cell was equipped with reflux condenser, graphite anode (15 × 25 × 5 mm, S = 3.75 cm^2) and a platinum plate cathode (15 × 25 × 5 mm, S = 3.75 cm^2) (see figure S1b in Supporting Information), and connected to a DC regulated power supply. A solution of (1-azidovinyl)benzene **1a** (0.5 mmol, 73 mg), *N*-hydroxyphthalimide **2** (1.0 mmol, 163 mg), radical scavenger – TEMPO, 1,1-diphenylethylene or BHT (1.0 mmol, 156-220 mg), pyridine (1.0 mmol, 79 mg) and [PyH]ClO_4 (0.5 mmol, 90 mg,) in 15.0 mL of acetone was electrolyzed using constant current conditions (i = 60 mA,

j_{anode} = 16 mA/cm^2) at 15 °C under magnetic stirring. After passing 1.1 F per mol **2** of electricity (reaction time 29 min), electrodes were washed with DCM (2 × 20 mL). The combined organic phases were concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), bath temperature ca. 50-55 °C. The yield of product **3a** was determined by ^{1}H NMR spectroscopy using *p*-methoxyacetophenone as the internal standard.

General Procedure for Cyclic Voltammetry

Cyclic voltammetry (CV) was implemented on an IPC-Pro M computer-assisted potentiostat manufactured by «Econix» (scan rate error 1.0%; potential setting 0.25 mV; scan rate 100 mV·s^{-1}). The experiments were performed in a 10 mL five-neck glass conic electrochemical cell with a water jacket for thermostatting. CV curves were recorded using a three-electrode scheme. In a typical case, 5 mL of a solution was utilized. The working electrode was a disc glassy-carbon electrode (d = 3 mm). A platinum wire served as an auxiliary electrode. An Ag/AgNO$_3$ electrode was used as the reference electrode and was linked to the solution by a porous glass diaphragm. The solutions were kept under thermally controlled conditions at 15±0.5 °C and deaerated by bubbling argon. Electrochemical experiments were performed under an argon atmosphere. The working electrode was polished before recording each CV curve.

General Procedure for Electron Paramagnetic Resonance (EPR)

The EPR spectra were recorded on Adani SPINSCAN X spectrometer in a X-band range (ν~9.43 GHz). The magnetic field modulation frequency was 100 kHz with 100 µT modulation amplitude. A quartz glass capillary tube (inner diameter 1.2 mm) was filled with a solution of *N*-hydroxyphthalimide (0.25M), pyridine (0.5M) and *n*-Bu$_4$NBF$_4$ (0.5M) in MeCN and equipped with a platinum wire anode and AgCl coated silver wire cathode (both 0.8 mm diameter), so that the interelectrode space is located in the working area of spectrometer. Wires were connected to PalmSens EmStat3+ potentiostat as follows: platinum wire − working electrode, silver wire − counter and reference electrode. Constant potential of 1V was applied for 30 s, and then spectra was recorded.

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FULL PAPER

Electrochemical Synthesis of *O*-Phthalimide Oximes from α-Azido Styrenes *via* Radical Sequence: Generation, Addition and Recombination of Imide-*N*-Oxyl and Iminyl Radicals with C-O / N-O Bonds Formation

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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