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Electrochemical Radical–Radical Cross-Coupling Approach between Sodium Sulfinates and 2*H*-Indazoles to 3-Sulfonylated 2*H*-Indazoles

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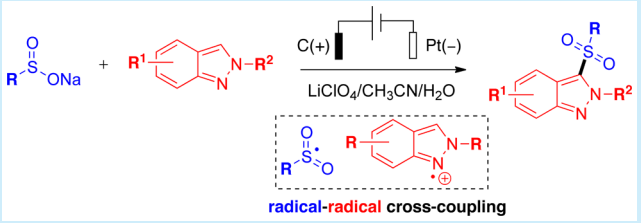
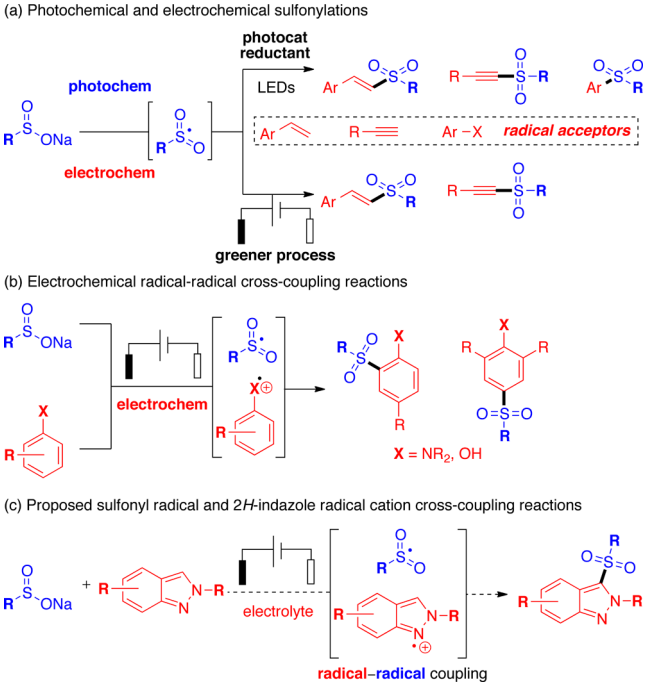
ABSTRACT: A direct cross-coupling between sodium sulfinates and 2*H*-indazoles has been developed under electrochemical conditions. The utilization of a graphite anode and platinum cathode in an undivided cell with a constant current of 7 mA allowed the concurrent oxidations of sulfinates and 2*H*-indazoles to sulfonyl radical and radical cationic 2*H*-indazoles, facilitating the direct radical–radical coupling strategy to 3-sulfonylated 2*H*-indazole derivatives. The transition-metal- and redox-reagent-free synthetic approach should serve as a valuable synthetic tool to achieve heteroaromatic compounds.



Given the wide biological activity of arylsulfonyl derivatives across a variety of disease states, the development of greener and efficient synthetic methods to heteroaromatic sulfonyl derivatives has been a long-term goal in organic synthesis.[1] While the oxidation of aryl sulfides and aryl sufoxides readily provides the desired sulfone moiety, the utilization of a separate oxidation step adds an extra tool in chemical process development. All things being equal, the chemical process for arylsulfonyl compounds is preferred to be convergent and to utilize a minimal amount of redox reagents and costly transition-metal catalysts. From this angle, sodium sulfinates fulfill the role of a dexterous sulfonyl source for alkenes,[2] alkynes,[3] and arenes[4] under photoredox catalysis (Scheme 1a). While the sulfonyl radical, generated under the photolytic conditions from sodium sulfinates, could be added to the unsaturated π bonds, the requirement of reductants for the photoredox processes deviates from the ideal chemical process development. In addition, the identification of a suitable photocatalyst to generate the sulfonyl radicals from sodium sulfates without quenching the excited state of photocatalyst by aromatic substrates[5] presents the difficulty associated with the inherent redox potentials of involved substrates.

Electrochemical synthesis allows the direct anodic oxidation of substrates without using redox reagents,[6] and the simple measurement of cyclic voltammetry of substrates provides the total amount of voltage required for the electrochemical oxidation processes (Scheme 1b). While sulfonyl hydrazides have been added to a few radical acceptors under the electrochemical conditions,[7] we envisioned the use of a greener sulfonyl radical source, sodium sulfinates for the synthesis of hetroaromatic sulfonyl derivatives. A noteworthy aspect of the current electrosynthetic approach is that, instead of utilizing radical acceptor coupling partners such as alkenes,[8]

Scheme 1. Sulfonyl Radical Generation and Addition to Unsaturated π Bonds



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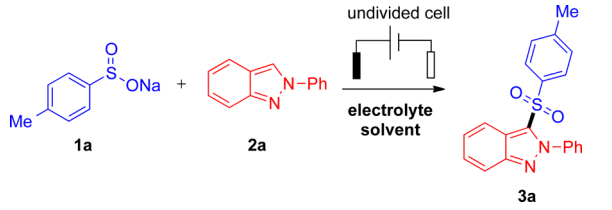
alkynes,[9] and indole,[10] the heteroaromatic compound, 2*H*-indazole,[11] is envisaged as a radical cationic species. The previous contributions by the Li group[12] and the Waldvogel group[13] utilized the electrochemical *ortho*- or *para*-C−H sulfonylation of anilines and phenols via the generation of radical cationic species from aniline and phenol derivatives. However, the utility of such radical−radical cross-coupling approaches to heteroaromtic compounds has not been investigated.[14] Thus, the prime goal of current electrosynthesis of 3-sulfonylated 2*H*-indazoles is not to use any chemical reagents other than electrolyte, $LiClO_4$, for the cross-coupling between electrochemically generated sulfonyl radicals and radical cationic heteroaromatic species.

To investigate the feasibility of electrochemical cross-coupling of sodium sulfinates and heteroaromatic compounds, the use of sodium *p*-toluenesulfinate **1a** and 2-phenyl-2*H*-indazole **2a** was chosen since our previous studies suggested that the oxidation potentials of sodium sulfinates[15] are similar to those of 2*H*-indazoles.[16] Indeed, the cyclic voltammetry measurements of sodium *p*-toluenesulfinate **1a** and 2-phenyl-2*H*-indazole **2a** indicated their oxidation potentials in 1.0−1.7 V (vide infra). Encouraged by the close oxidation potentials of sodium sulfinates and 2*H*-indazoles, a standard electrochemical reaction setup was applied to a 3:1 mixture of **1a** and **2a** in an undivided cell with constant current conditions (Table 1). Thus, the use of carbon rod anode and platinum plate cathode with the 4 mA current provided the desired 3-sulfonylated 2*H*-indazole **3a** in 59% yield (entry 1). When the current was changed to 7 and 10 mA (entries 2 and 3), the improved yield of **3a** was apparent in the 7 mA current to 72% (entry 2). Since no reaction was observed in the absence of electrolyte, the amount of electrolyte, $LiClO_4$, was varied (entries 4 and 5). It turned out that the use of 0.4 M $LiClO_4$ was optimal. The solvent screening revealed the inferior results in the MeOH/H_2O, DMA/H_2O, and DMF/H_2O mixtures (entries 6−8). In addition, the amount of water in the CH_3CN/H_2O mixture significantly influenced the yields of **3a** (entries 9 and 10), where the 1.3:1 ratio of CH_3CN/H_2O mixture provided the product **3a** in 20% (entry 10). The use of other electrolytes such as *n*-Bu_4ClO_4 and *n*-Bu_4BF_4 lowered the yields of **3a** to 37−44% (entries 11 and 12). When a carbon rod was used as both anode and cathode (entry 13) or a platinum plate as both anode and cathode (entry 14), the isolated yields of **3a** diminished to 14−26%. However, when the platinum plate cathode was replaced with a nickel plate rod (entry 15), a comparable yield of **3a** was observed at 63%. Our control experiments confirmed that the optimal use of sodium sulfinate **1a** was more than 3 equiv (entries 16 and 17) and the reaction did not take place under no current conditions (entry 18).

The optimized electrochemical cross-coupling reaction condition was applied to the various 2*H*-indazoles (Scheme 2). The electronic influence of the *N*-phenyl group of 2*H*-indazoles was minimal, providing the corresponding products **3a**−**3c** in 69−74% yields. However, the presence of a *tert*-butyl group and halogen atoms lowered the yields of products **3d**−**3i**, possibly due to the side reaction via electrochemical C_{sp2}−$C(CH_3)_3$ and C_{sp2}−halogen bond cleavages. Indeed, the CF_3 group-containing 2*H*-indzole **3g** was obtained in 32% yield, but the nitro-containing indazole **3h** could not be prepared under the electrochemical conditions. Nevertheless, the current electrochemical cross-coupling reaction tolerated methoxy **3k** and dimethyl group **3l**, providing the synthetically useful level of products. The electronic effect of 2*H*-indazoles

Table 1. Optimization of Electrochemical Cross-Coupling between Sodium Sulfinate and 2*H*-Indazole[a]



entry	(+)/(−) (mA)	electrolyte (M)	solvent	yield[b] (%)
1	C(+)-Pt(−) (4)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	59
2	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	72
3	C(+)-Pt(−) (10)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	56
4	C(+)-Pt(−) (7)	$LiClO_4$ (0.27)	CH_3CN/H_2O (2.5:1)	55
5	C(+)-Pt(−) (7)	$LiClO_4$ (0.53)	CH_3CN/H_2O (2.5:1)	52
6	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	MeOH/H_2O (2.5:1)	0
7	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	DMA/H_2O (2.5:1)	18
8	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	DMF/H_2O (2.5:1)	32
9	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (3:0.5)	71
10	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2:1.5)	20
11	C(+)-Pt(−) (7)	*n*-Bu_4ClO_4 (0.40)	CH_3CN/H_2O (2.5:1)	37
12	C(+)-Pt(−) (7)	*n*-Bu_4BF_4 (0.40)	CH_3CN/H_2O (2.5:1)	44
13	C(+)-C(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	26
14	Pt(+)-Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	14
15	C(+)-Ni(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	63
16[c]	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	63
17[d]	C(+)-Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	73
18	C(+)-Pt(−) (0)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	0

[a]Reaction using **1a** (0.33 mmol), **2a** (0.10 mmol), and electrolyte in solvent (M) in an undivided cell with constant current of 7 mA under argon for 2 h. [b]Isolated yield of **3a**. [c]Reaction using 2 equiv of **1a**. [d]Reaction using 4 equiv of **1a**.

was further investigated using 5-fluoro-2*H*-indazoles **3m**−**3o**, 5-chloro-2*H*-indazoles **3p** and **3q**, 6-methyl-2*H*-indazole **3r**, and 5,6-dioxolanyl-2*H*-indazole derivative **3s**.

The substrate scope of sodium sulfinates in the current cross-coupling reaction is illustrated in Scheme 3. The *para*-substituted benzenesulfinates readily participated in the reaction to give the desired products **3t**−**3z** in 35−71% yields. Among them, the 4-*tert*-butyl-substituted product **3v** and the 4-cyano-substituted product **3z** were obtained in 35−40% yields. However, the current electrochemical cross-coupling reaction did not tolerate the nitro group **3za** due to the preferential reduction capability of the nitro group. The presence of chlorine atom somewhat lowered the yields of products **3zb** and **3zc** to 32−48% yields. The substrate limitation of the current electrochemical cross-coupling reaction was apparent upon using 3-cyano-phenyl and naphthyl-substituted sulfinates, where the reaction stopped

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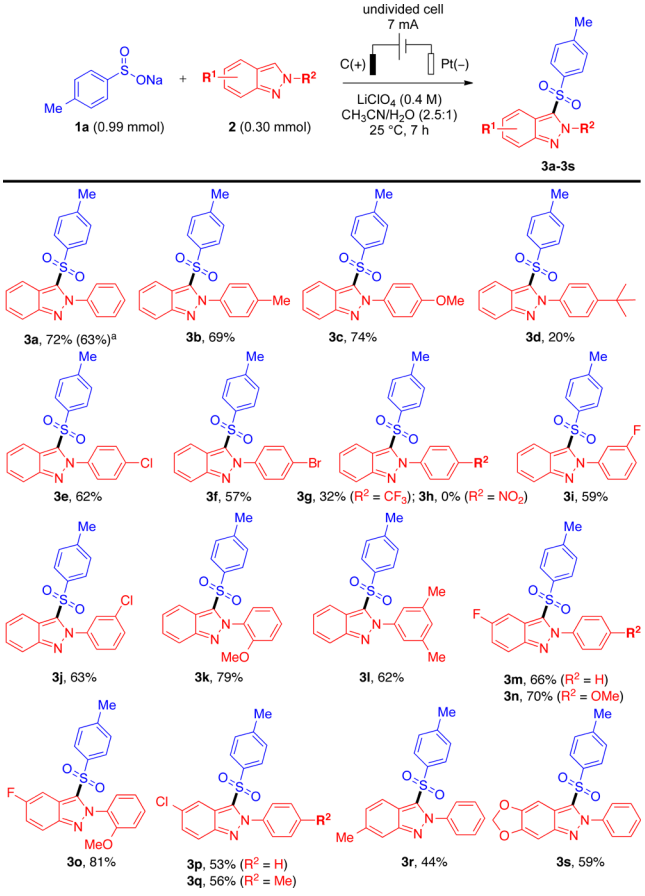
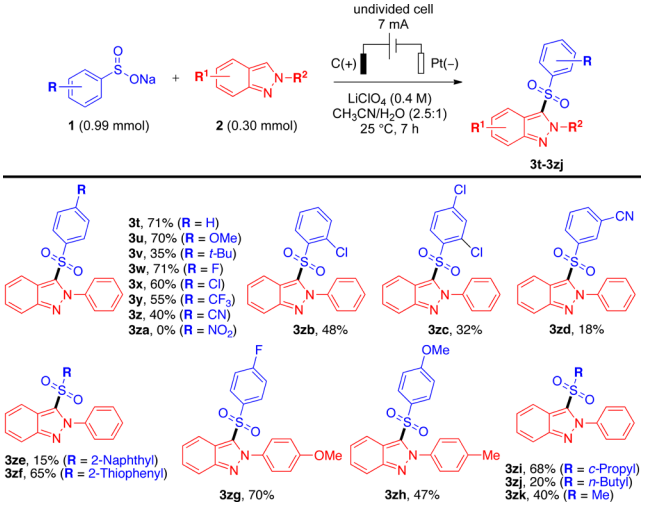
Scheme 2. Substrate Scope of Cross-Coupling between Sodium Sulfinate 1a and 2*H*-Indazoles



[a]Reaction in 1 mmol scale for 24 h.

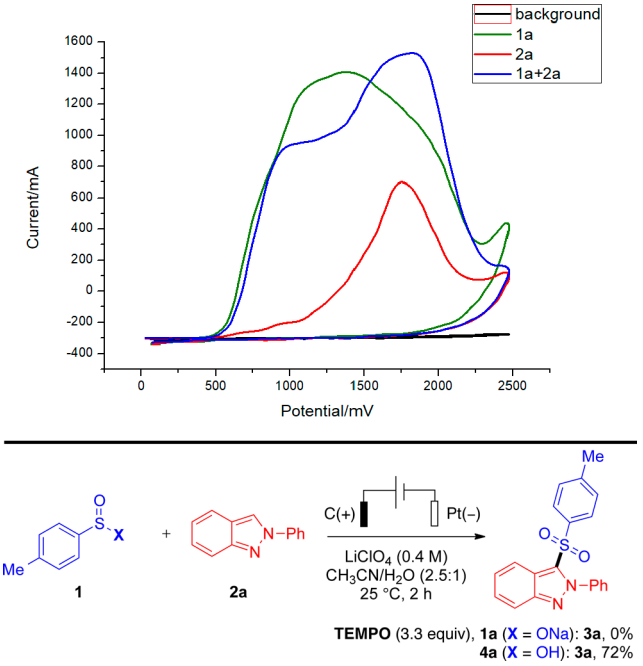
Scheme 3. Further Substrate Scope for Sodium Sulfinates and 2*H*-Indazoles



after <20% conversion to give **3zd** and **3ze** in 15−18% yields. The thiophenyl-substituted sulfinate was tolerated in the reaction to give the desired product **3zf** in 65% yield, and the electronically different sulfinates and 2*H*-indazoles provided **3zg** and **3zh** in 47−70% yields. The utilization of alkyl sulfinates was also possible, where the desired 3-sulfonylated-2*H*-indazoles **3zi**−**3zk** were obtained in 20−68% yields.

The mechanistic insight of the current electrochemical cross-coupling reactions has been obtained from the cyclic voltammograms (CV) of sodium *p*-toluenesulfinate **1a** and 2-phenyl-2*H*-indazole **2a** (Scheme 4). Thus, the sodium *p*-

Scheme 4. Cyclic Voltammograms and Control Experiments



toluenesulfinate **1a** was oxidized around 1.0 V (green curve), and the 2-phenyl-2*H*-indazole **2a** was oxidized at 1.7 V (red curve). The CV measurement of the reaction mixture indicated the two oxidation waves (blue curve), each corresponding to the respective reactant, **1a** and **2a**. The close oxidation potentials between sulfinates **1** and 2*H*-indazoles **2** appear to be critical in the radical−radical cross-coupling strategy since sodium naphthalene-2-sulfinates **1j** with lower oxidation potential of 0.7 V, opposed to **1a** with 1.0 V, provided the product **3ze** in a low yield of 15%.[17] Our control experiments confirmed no reaction in the absence of current or in the presence of a radical inhibitor, TEMPO. Also, the use of sodium sulfinates was not essential in this reaction since sulfinic acid **4a** equally worked to give the desired product **3a** in 72% yield. Nevertheless, the use of sodium sulfinates is more practical due to the enhanced stability over sulfinic acids in general.[18]

Scheme 5 illustrates the mechanistic proposal based on the CV measurements and control experimental data. Thus, it is reasonable to speculate the anodic oxidation of sulfinate **1** to the sulfonyl radical **A** under the electrochemical oxidation conditions. The soon-to-be followed oxidation of 2*H*-indazole **2** to the 2*H*-indazole radical cation **B** occurs at around 1.7 V. The radical−radical cross-coupling between **A** and **B** leads to the formation of cationic species **C** that in turn gives up a proton to give the product **3**. The cathodic reduction of protons to hydrogen gas completes the overall electrochemical cross-coupling of sulfinates and 2*H*-indazoles.

In summary, we have developed the electrochemical radical−radical cross-coupling strategy for the synthesis of 3-sulfonylated 2*H*-indazoles. The current transition-metal-free

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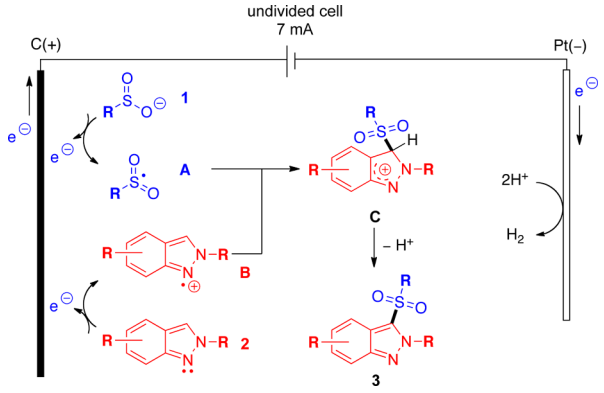
Scheme 5. Mechanistic Rationale for Radical−Radical Cross-Coupling Pathway



and redox-reagent-free synthetic approach to heteroaromatic compounds requires a simple electrochemistry setup without any added reaction components other than electrolyte. The present electrochemical synthesis of 3-sulfonylated 2*H*-indazoles has been conceived from the cyclic voltammograms of two starting materials: sodium sulfinates and 2*H*-indazoles. Given that the electrochemical experiment setups are widely available nowadays, the electrochemical radical−radical cross-coupling strategy should be applicable to the preparation of other heterocyclic compounds. We are currently pursuing the electrochemical synthesis of heterocycles of medicinal interest, and our results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02144.

Experimental procedures and characterization data for all new compounds, electrasyn reaction, electrochemical sulfonylation, mechanism study: cyclic voltammetry (CV), NMR Spectra (PDF)

FAIR data, including the primary NMR FID files, for compounds **1c−1e**, **1g−1p**, **2a−2r**, **3a−3g**, **3i−3z**, and **3zb−3zk** (ZIP)

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Notes

The authors declare no competing financial interest.

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