Catalyst-Controlled Selectivity in C–S Bond Formation: Highly Efficient Synthesis of C2- and C3-Sulfonylindoles

Yong Yang, Wanmei Li, Chengcai Xia, Beibei Ying, Chao Shen, and Pengfei Zhang*^[a]

Exploring a potential catalyst system for catalyst-controlled selectivity in C–S bond formation is a fascinating challenge. Herein, we described two novel and highly efficient methods for the selective synthesis of C2- and C3-sulfonylindoles showing good biological activities by employing iodide and copper catalysts, respectively. Mechanistic studies point to the crucial role of the electronic properties of the sulfonylated intermediates.

The development of suitable catalysts and conditions to promote a desired C–S bond-forming reaction is one of the fundamental challenges of catalysis.^[1] Recently, indole and its derivatives have aroused intense interest as privileged structural motifs for the pharmaceutical and agrochemical industries,^[2] C–S bonds attached to indoles have been recognized, because indole skeletons containing a sulfur moiety, in particular at the C2, C3, and N positions, are present in many biologically active molecules (Figure 1).^[3] Thus, the synthesis of sulfonylindoles



Figure 1. Selected drugs containing the sulfonylindole moiety.

through either construction or modification of indole rings by innovative methods has triggered attention in medicinal and synthetic chemistry. Although many useful methods of sulfonylation at the C2 and/or C3 position(s) of indoles have been reported that indirectly address these problems,^[4] direct synthetic methods for the regioselective formation of C2- and/or C3sulfonylindoles remain an elusive and unmet goal in synthetic chemistry. On the other hand, the elaboration of a strategy to control the site selectivity of indoles and the sulfur-containing segment is currently a serious concern.

Over the years, copper catalysts have been frequently used for synthetic organic chemistry;^[5] the use of copper salt catalysts has been shown to be successful, because copper possesses the ability to alter single- and double-electron quantities through transformation of its four oxidation states: Cu⁰, Cu¹, Cu^{II}, and Cu^{III}. Therefore, copper catalysts possess the ability to associate different functional groups through Lewis acid interactions or π coordination; this has been proven by many scientific experiments.^[5a]

Consequently, herein the copper-catalyzed 3-sulfonylation of indoles was successfully implemented through π coordination of 2C/3C-indole. Over the past few years, iodine-catalyzed systems have been proven to be powerful tools to form C–N, C–O, and C–S bonds,^[6] these systems have been employed in radical and ion reactions. In sharp contrast, iodide catalysts are less explored over the entire field of chemistry.^[7] The action of iodide in this reaction system is similar to that of iodine, but iodide is much gentler than iodine. Therefore, in terms of safety and efficiency of the catalyst system, the iodide-catalyzed reactions are significant for synthetic organic chemistry.

In recent years, major advances have been achieved in the C-H bond functionalization of indoles,^[3] unfortunately, the regioselective formation of C-S bonds at the C2 and/or C3 sites of indoles has not been explored much. For this purpose, we wanted to investigate the area immediately. Currently, sulfur compounds exist widely in nature, and sources of various sulfides for direct sulfonylation include organic and inorganic sulfides. Simultaneously, sulfide sources are frequently reported to have unstable, toxic, and odorous properties, and incorporation of these functional groups requires multiple synthetic steps with the generation of waste from reagents, solvents, and purification; furthermore, undesired byproducts are also produced. Therefore, we wanted to explore a way to attain the desirable requirement of atom economy^[8] and relative safety. To solve these problems and on the basis of our previous work on C-S couplings,^[9] we chose sodium sulfinates as a sulfonyl source. Sodium sulfinates are stable to air and moisture and are safe to humans; notably, the reaction generates environmentally benign byproducts, as we expected. During the course of our phased studies, we found that iodide and copper salt catalysts allow the direct formation of C2- and C3sulfonylindoles, respectively, through C-H functionalization of indoles. Above all, the two methods, which operate in air and in the presence of moisture, produce the products in excellent yields without the use of an excess amount of the sodium sulfinate and without a noble metal salt.

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 [[]a] Y. Yang, Dr. W. Li, Dr. C. Xia, B. Ying, Dr. C. Shen, Prof. P. Zhang College of Material, Chemistry and Chemical Engineering Hangzhou Normal University Hangzhou 310036 (P.R. China) E-mail: chxyzpf@hotmail.com

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Initially, indole (**1a**) and sodium 4-tolylsulfinate (**2a**) were used as the standard substrates under different conditions (Table 1). Originally, C3-sulfonylated indoles were thought to

Table 1. Optimization of the reaction conditions with the use of the copper salt catalyst. ^[a] $Catalyst (20 mol%)$ $Ligand (10 mol%)$ $Additive (1 equiv.)$ Solvent, air							
Entry	Catalyst [mol %]	Additive [equiv.]	Ligand [mol %]	Solvent	Yield [%] ^[b]		
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 ^(c) 16	CuCl Cul CuCl ₂ CuBr NiCl ₂ Pd(OAc) ₂ - CuCl CuCl CuCl CuCl CuCl CuCl CuCl Cu	KI KI KI KI KI PivOH KBr K ₂ S ₂ O ₈ K ₂ CO ₃ KI KI KI KI KI KI	- - - - - - - 2,2-dipyridyl PPh ₃ 1,10-phen 1,10-phen 1,10-phen	DMF DMF DMF DMF DMF DMF DMF DMF DMF DMF	63 44 42 53 trace 20 trace trace trace trace trace 46 72 86 (44 ^(d)) trace 45 trace		
17 18 19 20 21 22 [a] Cont (10 mol alic aci	CuCl CuCl CuCl CuCl CuCl ditions: 1a (1%), additive (d. [b] Yield of	KI KI KI KI I mmol), 2a 1 equiv.), sol isolated pro	1,10-phen 1,10-phen 1,10-phen 1,10-phen 1,10-phen 1,10-phen (1 mmol), cata vent (2 mL), 110 [°] oduct. [c] Perform	diglyme EtOH toluene anisole DMF lyst (20 mol C, air, 4 h; P ned under a	trace 15 15 trace trace 86 %), ligand ivOH = piv- N ₂ atmos-		

be synthesized. Assuming that a copper catalyst was needed, the first reaction was performed in the presence of CuCl (20 mol%) by using 1a (1 mmol) and 2a (1 mmol) as substrates, KI (1 equiv.) as an additive, and DMF (2 mL) as the solvent (Table 1, entry 1); fortunately, the desired product was acquired in 63% yield. Then, other catalysts including Cul, CuCl₂, CuBr, NiCl₂, and Pd(OAc)₂ were examined, in addition to some noncatalysts, but only moderate yields of the products were provided. Subsequently, adding ligands and various additives were examined. It was disappointing that some ligands and various additives generated poor yields. For comparison, if the additive was KI and the ligand was 1,10-phenantroline (1,10phen), the desired product was obtained in 86% yield (Table 1, entry 14). Subsequently, we performed the reaction under a nitrogen atmosphere with extraction of air (Table 1, entry 15), but the product was not detected. The effect of solvent was also investigated (Table 1, entries 16-21); the use of solvents such as DMSO, N-methylpyrrolidone (NMP), diglyme, EtOH, toluene, and anisole instead of DMF was less effective for this transformation. Therefore, the optimal conditions comprised the use of CuCl (20 mol%), 1,10-phenantroline (10 mol%), Kl (1 equiv.), and DMF (2 mL) at 110 °C in air for 4 h (Table 1, entry 14). During the course of screening the solvents, it is notable and surprising that an analogous organic compound was observed in 25% yield upon using Cul as the catalyst and AcOH as the solvent. Next, we did some trials to synthesize C2-sulfonylated indoles (Table 2). We surveyed various catalysts, including Cul, Nal, NH₄I, and Kl, in addition to no catalyst, and we found that NH₄I catalyzed the reaction most efficiently and increased the yield of corresponding product **4a** up to 65%. We also screened various oxidants, and the target com-

Table 2. Optin iodide catalyst	mization of the t. ^(a) + NaO ₂ S–Ph 2a	reaction condition Catalyst (10 mol%) Additive (1 equiv.) Solvent, air	ns with the us	se of the		
Entry	Catalyst	Additive	Solvent	Yield		
	[mol %]	[equiv.]		[%] ^[b]		
1	Cul	-	AcOH	25		
2	Nal	-	AcOH	37		
3	NH4I	-	AcOH	65		
4	KI	-	AcOH	40		
5	-	-	AcOH	trace		
6	NH4I	TBHP	AcOH	99		
7	NH₄I	DTBP	AcOH	90		
8	NH₄I	H_2O_2	AcOH	88		
9	NH₄I	AcOOH	AcOH	60		
10	NH₄I	ТВРВ	AcOH	67		
11 ^[c]	NH₄I	-	AcOH	8		
12 ^[d]	NH ₄ I	-	AcOH	trace		
[a] Conditions: 1a (1 mmol), 2a (1 mmol), catalyst (10 mol%), additive						

[a] Conditions: **1a** (1 mmol), **2a** (1 mmol), catalyst (10 mol%), additive (1 equiv.), solvent (2 mL), 60 °C, air, 2 h; DTBP=di-t-butyl peroxide, TBPB=tert-butyl perbenzoate. [b] Yield of isolated product. [c] Performed under a N₂ atmosphere. [d] 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO, 1 equiv.) was added.

pound was obtained in 99% yield with the aid of *tert*-butyl hydroperoxide (TBHP, 1 equiv.) and the NH_4I (10 mol%) catalyst.

According to our optimal conditions, the scope of the above-mentioned two systems for a variety of substrates was investigated. Indoles possessing both electron-donating substituents (e.g., $-CH_3$, -OH, and $-OCH_2Ph$) and electron-withdrawing substituents (e.g., -Br, -CN, -CHO, -COOCH₃, and -Cl) in the benzene ring of the indole tolerated the reaction conditions, and surprisingly, regardless of whether the substituent was installed in the ortho, meta, or para position of the indole, all substrates smoothly coupled to provide the products in good yields (Table 3). On the other hand, the influence of the electronic properties was subtle. Disappointingly, if iodide was used as the catalyst with indoles possessing an electron-withdrawing substituent (e.g., -CN, -COOCH₃) in the benzene ring, the corresponding products were not detected. For copper salt and iodide catalysts, the reactive points for the sulfonylation reaction are subtly different. The iodide and copper salt catalysts promote C2 and C3 sulfonylation if the C2 and C3 positions of the indole are free, respectively. Neverthe-

Table 3. Scope of the indoles.								
$ \begin{array}{c} R^{1} \stackrel{fi}{\amalg} \\ R^{1} \stackrel{fi}{\amalg} \\ H \\ 1 \end{array} \begin{array}{c} R^{1} \stackrel{fi}{\amalg} \\ R^{1} \stackrel{fi}{I} \stackrel{fi}{$								
Entry	R ¹	Ar	Yield [%] ^[a] 3 ^[b]	[]] (product) 4 ^[c]				
1	Н	$4-H_3CC_6H_4$	82 (3 a)	93 (4 a)				
2	4-CH ₃	$4-H_3CC_6H_4$	80 (3 b)	92 (4 b)				
3	5-CH ₃	$4-H_3CC_6H_4$	81 (3 c)	93 (4 c)				
4	6-CH ₃	$4-H_3CC_6H_4$	88 (3 d)	96 (4 d)				
5	7-CH₃	$4-H_3CC_6H_4$	89 (3 e)	97 (4 e)				
6	5-Br	$4-H_3CC_6H_4$	78 (3 f)	66 (4 f)				
7	5-CHO	$4-H_3CC_6H_4$	82 (3 g)	70 (4 g)				
8	5-OH	$4-H_3CC_6H_4$	76 (3 h)	82 (4 h)				
9	5-CN	$4-H_3CC_6H_4$	65 (3 i)	trace				
10	5-COOCH ₃	$4-H_3CC_6H_4$	72 (3 j)	trace				
11	5-OCH₂Ph	$4-H_3CC_6H_4$	80 (3 k)	90 (4 i)				
12	6-Cl	$4-H_3CC_6H_4$	88 (3 I)	91 (4j)				
13	$2-CH_3$	$4-H_3CC_6H_4$	75 (3 m)	90 (3 m)				
14	3-CH ₃	$4-H_3CC_6H_4$	n.r.	92 (4 k)				
15	Н	C ₆ H₅	86 (3 n)	99 (4 I)				
16	Н	4-CIC ₆ H ₄	70 (3 o)	98 (4 m)				
17	Н	$4-H_3COC_6H_4$	67 (3 p)	90 (4 n)				
18	Н	4-AcNHC ₆ H ₄	60 (3 q)	93 (4 o)				
19	Н		58 (3 r)	86 (4 p)				
20	Н	N	56 (3 s)	80 (4 q)				
21	Н	N O	70 (3 t)	77 (4 r)				
[a] Yield of isolated product. [b] Conditions: 1a (1 mmol), 2a (1 mmol), CuCl (20 mol%), 1,10-phenantroline (10 mol%), KI (1 equiv.), DMF (2 mL), 110 °C, air, 4 h; n.r.=no reaction. [c] Conditions: 1a (1 mmol), 2a (1 mmol), NH _a I (10 mol%), TBHP (1 equiv.), ACOH (2 mL), 60 °C, air, 2 h.								

less, if the C2 position is occupied by a substituent, the iodide and copper salt catalysts both promote reaction at the C3 position of the indole ring. In contrast, if the C3 position of the indole is occupied, regretfully, only the KI catalyst can perform sulfonylation at the C2 position of the indole. However, the result offers powerful testimony as to which reaction site has priority under iodide and copper salt catalysis. We also evaluated substituent effects of the sodium sulfinates; explicitly, $4-ClC_6H_4$, $4-CH_3OC_6H_4$, $4-AcNHC_6H_4$, 2-naphthyl, 8-quinolinyl, 4-(3,5-dimethyl-1,2-oxazole), and unsubstituted sodium sulfinates were utilized for the coupling reaction, and all underwent smooth coupling with the indole to give the products in moderate to excellent yields with extremely high regioselectivity.

Subsequently, we also investigated the reactions mechanism. On the basis of our results (Scheme 1) and literature reports,^[10] two plausible mechanisms are proposed. Initially, the outcome of the Cu-catalyzed mechanism is illustrated (Scheme 2). From observation of the experiment results, oxygen is necessary for the copper-catalyzed reaction. With the aid of oxygen, Cu^I is transformed into Cu^{II} and gains the ability to associate with the indole through π coordination to form copper complex [I].

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Scheme 1. Control experiments.



Scheme 2. Proposed mechanism with the copper catalyst.

A molecule of HX is lost molecule though electrophilic addition to generate copper complex [II]. Then, interchange of the anion between copper complex [II] and the sodium sulfinate occurs to form copper complex [III]. Finally, the reaction cycle is closed with the aid of oxygen.

The iodide-catalyzed mechanism was also investigated (Scheme 3). Initially, HI is formed by reaction of the iodide with acid. It is speculated that HI decomposes at a suitable temperature, and on the basis of this conjecture, hydrogen and an iodide radical emerge, because if the reaction is performed without TBHP, the target product will be deoxidized and the reaction mixture turns purple, which might suggest the formation of hydrogen and I₂. On the basis of literature reports by Lei^[10g] and co-workers and our control experiments, the sulfinate anion is activated by O₂ to form an oxidative radical molecule; this was proved by our trial experiments (Scheme 3). Then, the sulfonate radical associates with the iodide radical to form RSO₂I. Finally, nucleophilic attack of RSO₂I at the C2 position of the indole is accompanied by loss of HI, which leads to the formed target product.

In summary, we presented an unprecedented regioselective sulfonylation reaction of indoles with sodium sulfinates through electrophilic addition to copper and nucleophilic attack of *p*-toluenesulfonyl iodides. The two facile and efficient

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Scheme 3. Proposed mechanism with the iodide catalyst.

strategies use copper salt and iodide catalysts, respectively, and our method features easy operation, excellent yields, and cheap catalysts. The current investigation gave significant directive to promote further study of synthetic regioselectivity.

Experimental Section

General procedure for the synthesis of 3-sulfonylindoles 3

A mixture of the (un)substituted indole (1 mmol), (un)substituted sodium sulfinate (1 mmol), CuCl (20 mol%), 1,10-phen (10 mol%), and Kl (1 equiv.) in DMF (2 mL) was stirred in air at 110 °C for 6 h. Then, the mixture was extracted with CH_2Cl_2 (10 mL) and water (20 mL), the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (5 mL). The combined organic layer was dried with anhydrous Na_2SO_4 , and the solution was then concentrated under reduced pressure. The product was purified by flash column chromatography (200–300 mesh silica gel, petroleum ether/ethyl acetate = 5:1).

General procedure for the synthesis of 2-sulfonylindoles 4

A mixture of the (un)substituted indole (1 mmol), (un)substituted sodium sulfinate (1 mmol), NH₄I (10 mol%), and TBHP (1 equiv.) in AcOH (2 mL) was stirred in air at 60 °C for 2 h. Then, the mixture was extracted with CH_2CI_2 (10 mL) and water (20 mL), the organic phase was separated, and the aqueous phase was extracted with CH_2CI_2 (5 mL). The combined organic layer was dried with anhydrous Na₂SO₄, and the solution was concentrated under reduced pressure. The product was purified by flash column chromatography (200–300 mesh silica gel, petroleum ether/ethyl acetate = 15:1).

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