EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: NaI-Catalyzed Oxidative Amination of Aromatic Sodium Sulfinates: Synergetic Effect of Ethylene Dibromide and Air as Oxidants

Authors: Ying Fu, Quan-Zhou Li, Qin-Shan Xu, Helmut Hügel, Ming-Peng Li, and Zhengyin Du

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201801386

Link to VoR: http://dx.doi.org/10.1002/ejoc.201801386

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

10.1002/ejoc.201801386

WILEY-VCH

NaI-Catalyzed Oxidative Amination of Aromatic Sodium Sulfinates: Synergetic Effect of Ethylene Dibromide and Air as Oxidants

Ying Fu,*[a] Quan-Zhou Li[a], Qin-Shan Xu[a], Helmut Hügel[b], Ming-Peng Li[a] and Zhengyin Du[a]

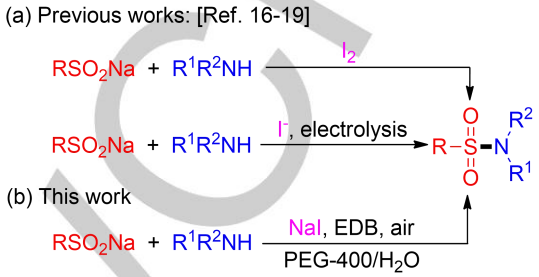
Dedication ((optional))

Abstract: A novel NaI-catalyzed oxidative amination of sodium sulfinates, employing both ethylene dibromide (EDB) and air as the oxidants, is described. EDB was first demonstrated to be a promising mild organic oxidant that in air, converted NaI into molecular iodine to promote the cross-coupling reactions of aromatic sodium sulfinates with amines to produce arylsulfonamides. Mechanistic studies indicated that a radical pathway might be involved in the reaction process.

Introduction

The importance of sulfonamide containing drugs, also called sulfa drugs,[1] has attracted much attention on the construction of this privileged structural motif. Traditionally, sulfonamides are prepared *via* coupling of sulfonyl chlorides with amines.[2] However, the harsh reaction conditions associated with sulfonyl chlorides preparation, e.g., use of hazardous chlorine reagents such as aqueous chlorine,[3] $SOCl_2$[4] and SO_2Cl_2,[5] limited the accessibility of some highly functionalized sulfonyl chlorides. Thus, complementary methodologies, especially these employing bench-stable, nonhygroscopic sodium sulfinates[6] as the sulfonylating agents have been extensively developed in recent years. Notably, Jiang and co-workers first reported in 2013 an efficient synthesis of sulfonamides *via* copper-catalyzed aerobic oxidative coupling of sodium sulfinates with amines.[7] The amine substrate was further expanded to O-benzoyl hydroxylamines, azoles and other amine derivatives.[8]

Molecular iodine was recognized as a transition metal surrogate to catalyze, or as a selective environmentally friendly oxidant, to perform a wide range of coupling reactions of sodium sulfinates with, e.g. imidazopyridines,[9] alkynes,[10] cinnamic acids,[11] 1,3-dicarbonyl compounds,[12] enol acetates,[13] benzotriazoles[14] and NH-1,2,3-triazoles[15] etc. Recently, Yotphan[16] et al. disclosed an efficient iodine-catalyzed, sodium percarbonate participated oxidative amination of sodium sulfinates whereby sulfonamides were prepared in good yields. Concomitantly, two communications from Song and Yuan[17] groups respectively reported that molecular iodine alone could efficiently promote the coupling reactions of sodium sulfinates and amines. Furthermore, the



Scheme 1. I_2/I- mediated coupling of sodium sulfinates with amines.

combination of molecular iodine and TBHP (*tert*-butyl hydroperoxide) could initiate *N*-dealkylative coupling of tertiary amines with sodium sulfinates.[18] These procedures are advantageous in that the coupling reactions were carried out in water under metal-free conditions. However, considering to the volatility and toxicity of molecular iodine or the excessively employed explosive peroxide, these protocols still have shortcomings in large scale syntheses, especially in industry sulfonamide pharmaceutical syntheses. Very recently, several greener electrochemical routes[19] employing metal iodide as the redox catalyst, for the cross-coupling of sodium sulfinates and amines, were developed (Scheme 1a). These excellent advances on S-N coupling reactions as well as our interests on developing greener and practical methods for the synthesis of sulfur containing compounds[20] prompted us to present here the milder NaI-catalyzed ethylene dibromide (EDB) and air co-oxidized coupling reactions of sodium sulfinates with amines whereby good to high yields of sulfonamides can be obtained (Scheme 1b).

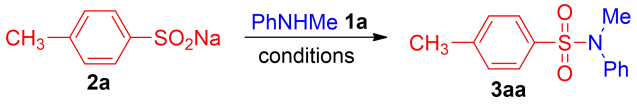
Results and Discussion

Initially, the coupling reaction between *N*-methylaniline (**1a**, 1.0 mmol) and sodium *p*-toluene sulfinate (**2a**, 1.5 mmol) was chosen as the model reaction system. Gratifyingly, when the reaction was conducted in the presence of a catalytic amount of NaI (0.3 mmol, 20 mol% with respect to sodium sulfinate **2a**) and EDB (3.0 mmol, 2.0 molar equivalents with respect to sodium sulfinate **2a**) at 60 °C for 8h, the desired compound **3aa** was isolated in 36% yield (Table 1, entry 1). Without NaI or EDB, sulfonamide **3aa** was not formed (entries 2 & 3). Solvent screening (Table 1, entries 4-13) showed that when the reaction was carried out in PEG-400/H_2O (2 mL, 1:1, v/v) the highest yield of sulfonamide **3aa** (entry 13) was produced. Previously, EtOH was demonstrated as an ideal solvent in I_2 mediated cross-coupling reactions between sodium sulfinates and amines.[17a] However, in our reaction protocol, it was an

[a] Dr. Y. Fu, Q.-Z. Li, Q.-S. Xu, M.-P. Li and Prof. Dr. Z. Du
College of Chemistry and Chemical Engineering
Northwest Normal University, Lanzhou, 730070, China
E-mail: fu_yingmail@126.com
[b] Assoc. Prof. H. Hügel
College of Science, Engineering & Health, School of Science,
ACES, RMIT University, Melbourne, 3001, Australia.

Supporting information for this article is given via a link at the end of the document.

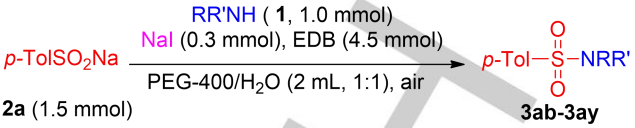
Table 1. Optimization of reaction conditions [a]



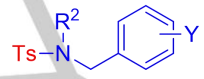
Entry	Iodide	Solvent	Yield [b]/%
1	NaI	DMF	36
2	-	DMF	No reaction
3	NaI	DMF	No reaction [c]
4	NaI	DMA	52
5	NaI	DMSO	62
6	NaI	EtOH	43
7	NaI	DCE	17
8	NaI	Anisole	43
9	NaI	1,4-Dioxane	31
10	NaI	Toluene	24
11	NaI	DMF/H_2O	68
12	NaI	H_2O	56
13	NaI	PEG-400/H_2O	82
14	NaI	PEG-400/H_2O	42[d]
15	KI	PEG-400/H_2O	80%
16	NH_4I	PEG-400/H_2O	76
17	CuI	PEG-400/H_2O	31
18	NaI	PEG-400/H_2O	67 [e]

[a] Reaction conditions: A mixture of **1a** (1.0 mmol), **2a** (1.5 mmol), iodides (0.3 mmol) and EDB (3.0 mmol) in designated solvent (2 mL) was heated to 60 °C under air for 8 h. [b] Isolated yields. [c] EDB was not used. [d] 1.5 mmol of EDB was employed. [e] Under nitrogen atmosphere.

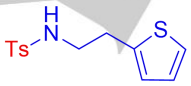
Table 2. Substrate scope of amines [a]



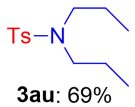
3ab:	R^1 = Me,	X = 3-Me,	71%
3ac:	R^1 = Me,	X = 4-Me,	80%
3ad:	R^1 = H,	X = 2-Me-4-Cl,	63%
3ae:	R^1 = H,	X = 4-Me	82%
3af:	R^1 = H,	X = 2-*i*Pr,	43%
3ag:	R^1 = H,	X = 4-OMe	73%
3ah:	R^1 = H,	X = 4-OCF_3,	66%
3ai :	R^1 = H,	X = 3-MeS,	57%
3aj:	R^1 = H,	X = H,	78%
3ak:	R^1 = H,	X = 4-F	74%
3al:	R^1 = H,	X = 4-Cl,	76%
3am:	R^1 = H,	X = 3-Cl-4-F,	74%
3an:	R^1 = H,	X = 4-Br,	78%
3ao:	R^1 = H,	X = 4-I,	73%
3ap:	R^1 = H,	X = 3-CF_3,	59%



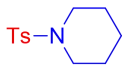
3aq:	R^2 = H,	Y = H, 75%
3ar:	R^2 = H,	Y = 4-F, 63%
3as:	R^2 = Me,	Y = 3-F, 61%



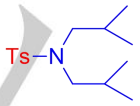
3at: 66%



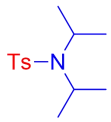
3au: 69%



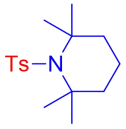
3av: 72%



3aw: 58%



3ax: trace



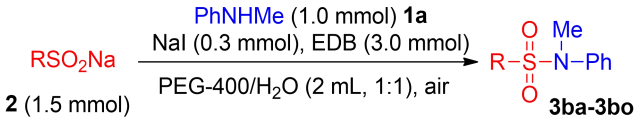
3ay: 0%

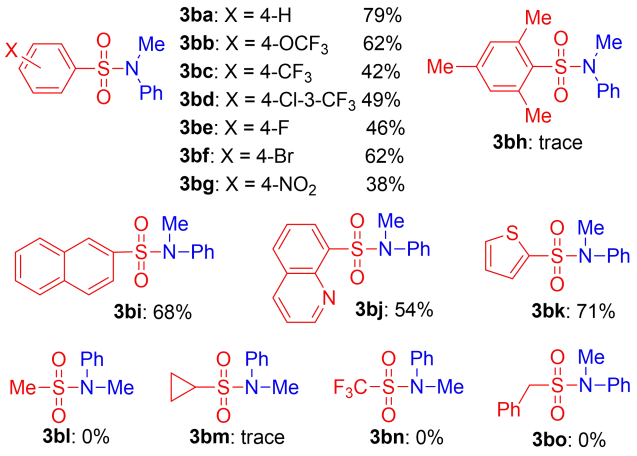
[a] Isolated yields based on amines **1**.

unsatisfactory solvent, since a significant amount of TsOEt was formed, affording only 43% yield of **3aa** (entry 6). The employment of water[17b] alone as solvent, due to the poor solubility of methylaniline **1a**, provided a lower yield of product **3aa** (56%, entry 12). Decreasing the amount of EDB to 1.5 mmol resulted in a significant reduction on the yield of **3aa** (42%, entry 14). Other iodides screened did not improve the yield of **3aa** further (entries 15-17). Moreover, performing this reaction under a nitrogen atmosphere led to a lower yield of **3aa**. In this case, a significant amount of *N,N'*-dimethyl-*N,N'*-diphenylhydrazine, derived from the homocoupling of *N*-methylaniline **1a** was generated (entry 18).

With the optimized conditions in hand, the substrate scope of amines was first investigated employing sodium *p*-tolylsulfinate **2a** as the model substrate (Table 2). Anilines and *N*-methylanilines bearing either electron-donating groups (Me, *i*Pr, OMe and OCF_3) or electron-withdrawing groups (F, Cl, Br, I and CF_3) reacted smoothly with **2a** to give the corresponding *p*-tolylsulfonamide products in good yields (Table 2, **3ab-3ap**). *N*-Methylanilines exhibit similar reactivity to primary anilines in terms of reaction rates and yields of sulfonamide products. Steric constraints on the phenyl rings of anilines significantly affected the yields of sulfonamides as the reactions of *ortho*-substituted anilines (2-*i*Pr and 2-Me) produced relatively lower yields of sulfonamides (**3ad** & **3af**). Remarkably, the peroxide-sensitive substituent, *viz*. SCH_3, was tolerated under these reaction conditions (**3ai**), suggesting an advantage of our protocol over the previously reported method.[16] Primary and secondary aliphatic amines (including benzylic amines) all react with **2a** under these optimized reactions, giving the corresponding sulfonamides (**3aq-3aw**) in moderate to good yields. Steric hindered aliphatic secondary

Table 3. Substrate scope of sodium sulfinates[a]





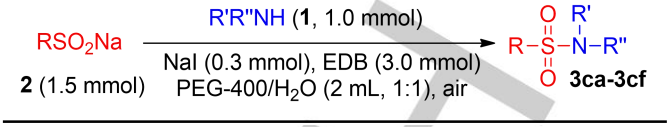
[a] Isolated yields based on amines **1a**.

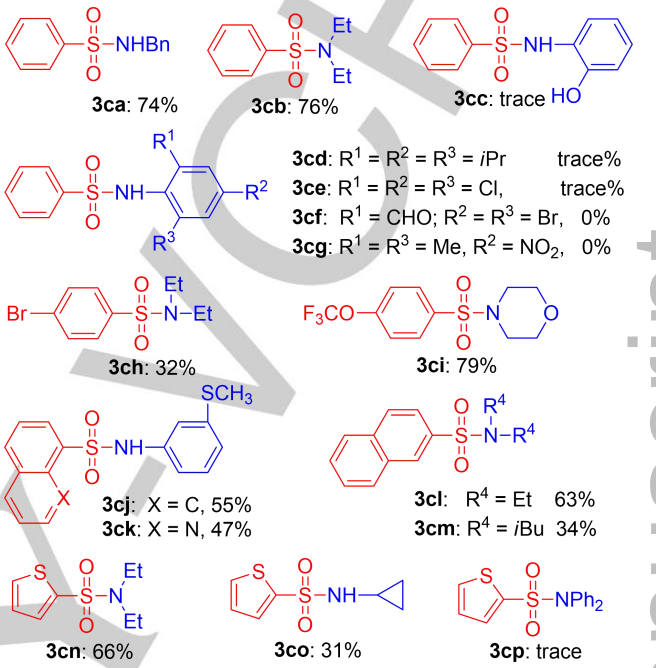
amines, *viz.*, diisopropylamine and 2,2,6,6-tetramethylpiperidine, do not react with **2a** at all (**3x** & **3y**).

The scope of sodium sulfinates was then investigated by reactions with *N*-methylaniline (**1a**) under our experimental conditions. As shown in Table 3, both electron-rich and electron-deficient aromatic substituents on the sodium sulfinates were tolerant under the novel transformation (Table 3, **3ba-3bi**). However, the latter reactions generally gave lower product yields than the former, that may be attributed to the electron-withdrawing inductive effect. The steric constraints imposed by the substituents on aromatic rings of sodium benzenesulfinates are the dominant influences on the yields of sulfonamides as the highly sterically hindered sodium 2,4,6-trimethylbenzenesulfinate substrate was unreactive (**3bh**). Heteroaryl sulfinates as represented by sodium quinoline-8-sulfinate and sodium thiophene-2-sulfinate also afforded the corresponding sulfonamides (**3bj** & **3bk**) in acceptable yields. Unfortunately, the aliphatic sodium sulfinates that were screened failed to yield the corresponding products (**3bl-3bo**), possibly because the unstability of aliphatic sulfonyl radicals under these reaction conditions.[21]

Further exploration of this protocol with different arylsulfinates and amines (Table 4) showed that aliphatic amines including benzylamine (**3ca**), diethylamine (**3cb**, **3ch**, **3cl** & **3cn**), cyclopropylamine (**3co**) and morpholine (**3ci**) all reacted to generate the corresponding sulfonamides. Reactions of peroxide sensitive 3-methylthioaniline with sodium 2-naphthylsulfinate and sodium quinoline-8-sulfinate afforded the corresponding sulfonamides (**3cj** & **3ck**) in moderate yields. Highly sterically hindered arylamines including 2,4,6-triisopropylaniline, 2,4,6-trichloroaniline, 2-amino-3,5-dibromobenzaldehyde and 2,6-dimethyl-4-nitroaniline were unreactive (**3cd-3cg**). Unexpectedly, 2-hydroxyaniline did not

Table 4. Substrate scope of sodium sulfinates and amines [a]

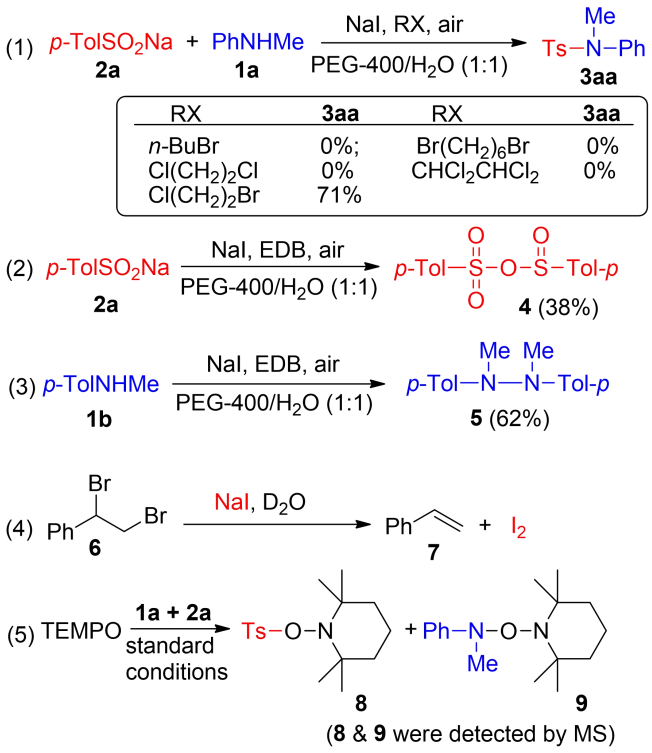




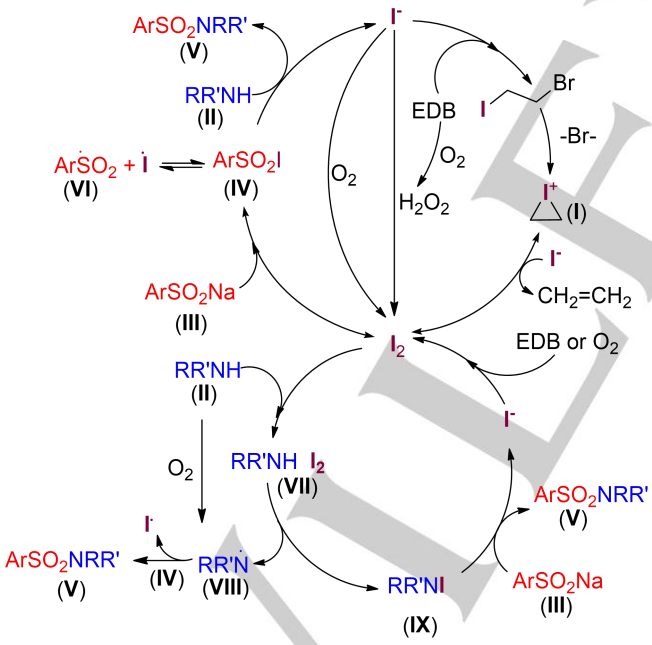
[a] Isolated yields based on amines **1a**.

react with sodium benzenesulfinate (**3cc**), possibly because the intramolecular hydrogen bond formed between the OH and NH$_2$ groups that weakened the nucleophilicity of the amino group. Attempts to prepare the diphenylamine-sulfonamide (**3cp**) were unsuccessful.

Control experiments were performed in order to elaborate and gain insight into the reaction mechanism (Scheme 2). Firstly, replacement of EDB with *n*-BuBr, 1,6-dibromohexane, ethylene dichloride or acetylene tetrachloride did not initiate the desired sulfonamide **3aa** in a comparable yield to that of EDB (Scheme 3, eqn1). When only sodium *p*-tolylsulfinate **2a** (without **1a**) was reacted, compound **4** was isolated in 38% yield that may be produced *via* capture of the *in situ* formed sulfonyl iodide[16] from sodium sulfinate **2a** (eqn 2). On the other hand, when *N*-Methyl-*p*-toluidine **1b** (without **2a**) was reacted, the dimer 1,2-dimethyl-1,2-di-*p*-tolylhydrazine (**5**) was the only product isolated in 62% yield (eqn 3), suggesting that **1b** in the reaction conditions formed a radical intermediate. ^{1}H NMR analysis of the crude reaction mixture of stilbene dibromide (**6**) and NaI in D_2O in air showed that styrene (**7**) was generated. Notably, the color of all these reactions involving NaI and EDB, when heated up to 60 °C, changed gradually into brown red which may be ascribed to the in situ generated I_2 (eqn 4).[22] Finally, when a radical trapping agent TEMPO (2 equiv.) was added into the model reaction of **1a** and **2a**, the yield of **3aa**



Scheme 2. Control experiments.



Scheme 3. Proposed reaction mechanism.

dramatically dropped to 35%. Adducts **8** and **9** were detected by ESI-MS, demonstrating the occurrence of both amine radical and sulfonyl radical (eqn 5).

Based on the outcomes of these control reactions, a plausible reaction mechanism is proposed (Scheme 3). First, the I/Br exchange reaction[24] with EDB produced 1-bromo-2-iodoethane that after elimination of bromide *via* intramolecular S_N2 substitution, generated a cyclopropa-iodinium cation (**I**) which was immediately trapped by an iodine anion to form ethene and I_2. The reaction of $ArSO_2Na$ (**III**) with I_2 generates the reactive sulfonyl iodide (**IV**).[25] Displacement of sulfonyl iodide (**IV**) with amine (**II**) produces the sulfonamide product (**V**), regenerating the iodine anion. Decomposition of sulfonyl iodide species yields a sulfonyl radical (**VI**) and an iodine radical.[16] Additionally, amine (**II**) could be oxidized by O_2,[26] or more likely, first combine with molecular iodine to form an amine-iodine complex[27] (**VII**). Decomposition of **VII** yields a nitrogen-centered radical (**VIII**)[28] which combined with sulfonyl iodide (**IV**) to form the sulfonamide product (**V**). Furthermore, **VII** could form the iodo-amine intermediate **IX**, which reacts with sodium sulfinate (**III**) to produce the sulfonamide product (**V**). Another possibility is that the mixture of EDB with O_2 produces H_2O_2[29] that could oxidize the iodide anion to form molecular iodine that enhances the reaction rate.

Conclusions

This work represents the first systematic investigation of NaI catalyzed oxidative cross-coupling reactions of aromatic sodium sulfinates with primary/secondary amines to produce sulfonamides. The coupling reagents are catalytic NaI, air and EDB that was found to be a mild organic oxidant. EDB with air converted NaI into *in situ* I_2 that then promoted/facilitated the cross-coupling reactions of both sulfinateand amine radical intermediates. Various types of sulfonamides could be generated in moderate to good yields. Compared with previous works, this study illustrates catalytic simplicity, environmental friendliness, low-cost and tolerance of a wide range of functional groups.

Experimental Section

General

All reactions were performed in Schlenck tubes under air. ^1H (400 or 600 MHz), ^{13}C (101 or 151 MHz) spectra were recorded in $CDCl_3$ solutions. Flash chromatography was performed on silica gel (300-400 mesh). Sodium sulfinates and amines were obtained commercially and used as supplied.

Synthesis of sulfonamides

To a 10 mL Schlenk tube equipped with a stirring bar, sodium sulfinate **2** (1.5 mmol), amine **1** (1.0 mmol), NaI (45 mg, 0.3 mmol), EDB (564 mg, 260 μL, 3.0 mmol), PEG-400 (1.0 mL) and water (1.0 mL) were added and the reaction mixtures were heated to 60 °C under air for 8 h. After cooling to ambient temperature, the reaction product was dissolved in dichloromethane (10 mL) and washed successively with water (2×10 mL) and then brine (10 mL). The aqueous phase was further extracted with dichloromethane (10 mL) and washed as previously. The organic phase was combined, dried over Na_2SO_4 and concentrated. Purification by silica gel column chromatography gave the product sulfonamides.

Acknowledgments

The authors are grateful for financial support from the National Natural Science Foundation of China (No. 21762040, 21262030).

Keywords: Ethylene dibromide • NaI • Oxidative coupling • Sodium sulfinates • Sulfonamide

[1] J. Drews, *Science* **2000**, *287*, 1960-1964.

[2] a) M. Harmata, P. Zheng, C. Huang, M. G. Gomes, W. Ying, K.-O. Ranyanil, G. Balan, N. L. Calkins, *J. Org. Chem*. **2006**, *72*, 683-685; b) R. Sridhar, B. Srinivas, V. P. Kumar, M. Narender, K. R. Rao, *Adv. Synth. Catal*. **2007**, *349*, 1873-1876; c) J. Ji, Z. Liu, P. Liu, P. Sun, *Org. Biomol. Chem*. **2016**, *14*, 7018-7023.

[3] a) V. Percec, T. K. Bera, B. B. De, Y. Sanai, J. Smith, M. N. Holerca, B. Barboiu, B. B. B. Grubbs, J. M. J. Fréchet, *J. Org. Chem*. **2001**, *66*, 2104-2117; b) R. J. Watson, D. Batty, A. D. Baxter, D. R. Hannah, D. A. Owen and J. G. Montana, *Tetrahedron Lett*. **2002**, *43*, 683-685.

[4] a) S. O. Alapafuja, S. P. Nikas, V. G. Shukla, I. Papanastasiou, A. Makriyannis, *Tetrahedron Lett.* **2009**, *50*, 7028-7085; b) K. Bahrami, M. M. Khodaei, M. Soheilizad, *J. Org. Chem*. **2009**, *74*, 9287-9291.

[5] a) R. Pandya, T. Murashima, L. Tedeschi, A. G. M. Barret, *J. Org. Chem*. **2003**, *68*, 8274-8276; b) H. Woolven, C. González-Rodrígues, I. Marco, A. L. Thompson, M. C. Willis, *Org. Lett.* **2011**, *13*, 4876-4878; c) L. G. Monovich, R. A. Tommasi, R. A. Fujimoto, V. Blancuzzi, K. Clark, W. D. Cornell, R. Doti, J. Doughty, J. Fang, D. Farley, J. Fitt, V. Ganu, R. Goldberg, R. Goldstein, S. Lavoie, R. Kulathila, W. Macchia, D. T. Parker, R. Melton, E. O'Byrne, G. Pastor, T. Pellas, E. Quadros, N. Reel, D. M. Roland, Y. Sakane, H. Singh, J. Skiles, J. Somers, K. Toscano, A. Wigg, S. Zhou, L. Zhu, W. Shieh, S. Xue, L. W. McQuire, *J. Med. Chem*. **2009**, *52*, 3523-3538.

[6] a) X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun*. **2013**, *49*, 6102-6104; b) J. Aziz, S. Messaoudi, M. Alami, A. Hamze, *Org. Biomol. Chem*. **2014**, *12*, 9743-9759; c) Y. Fu, Q.-S. Xu, Q.-Z. Li, Z. Du, K.-H. Wang, D. Huang, Y. Hu, *Org. Biomol. Chem*. **2017**, *15*, 2841-2845.

[7] X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun*. **2013**, *49*, 6102-6104.

[8] a) H. Zhu, Y. Shen, Q. Deng, T. Tu, *Chem. Commun*. **2015**, *51*, 16573-16576; b) H. Zhu, Y. Shen, Q. Deng, C. Huang, T. Tu, C*hem. Asian J.* **2017**, *12*, 706-712; c) L. Fu, X. Bao, S. Li, Li. Wang, Z. Liu, W. Chen, Q. Xia, G. Liang, *Tetrahedron* **2017**, *73*, 2504-2511; d) S.-X. Wu, Y.-K. Zhang, H.-W. Shi, J. Yan, *Chin. Chem. Lett.* **2016**, *27*, 1519-1522; e) X. Bao, X. Rong, Z. Liu, Y. Gu, Q. Xia, *Tetrahedron Lett*. **2018**, *59*, 2853-2858.

[9] Y.-J. Guo, S. Lu, L.-L. Tian, E.-L. Huang, X.-Q. Hao, X. Zhu, T. Shao, M.-P. Song, *J. Org. Chem*. **2018**, *83*, 338-349.

[10] Y. Sun, A. Abdukader, D. Lu, H. Zhang, C. Liu, *Green Chem*. **2017**, *19*, 1255-1258.

[11] J. Gao, J. Lai, G. Yuan, *RSC Adv*. **2015**, *5*, 66723-66726.

[12] X.-J. Pan, J. Gao, G.-Q. Yuan, *Tetrahedron* **2015**, *71*, 5525-5530.

[13] V. K. Yadav, V. P. Srivastava, L. D. S. Yadav, *Tetrahedron Lett*. **2016**, *57*, 2236-2238.

[14] S.-X. Wu, Y.-K. Zhang, H.-W. Shi, J. Yan, *Chin. Chem. Lett.* **2016**, *27*, 1519-1522.

[15] R. J. Reddy, A. Shankar, M. Waheed, J. B. Nanubolu, *Tetrahedron Lett*. **2018**, *59*, 2014-2017.

[16] a) C. Buathongjan, D. Beukeaw, S. Yotphan, *Eur. J. Org. Chem.* **2015**, *2015*, 1575-1582; b) J. Zhao, J. Xu, J. Chen, X. Wang, M. He, *RSC Adv.* **2014**, *4*, 64698-64701.

[17] a) K. Yang, M. Ke, Y. Lin, Q. Song, *Green Chem*. **2015**, *17*, 1395-1399; b) X. Pan, J. Gao, J. Liu, J. Lai, H. Jiang, G. Yuan, *Green Chem*. **2015**, *17*, 1400-1403; c) W. Wei, C. Liu, D. Yang, J. Wen, J. You, H. Wang, *Adv. Syn. Catal*. **2015**, *357*, 987-992.

[18] a) J. Lai, L. Chang, G. Yuan, *Org. Lett*. **2016**, *18*, 3194-3197; b) R. J. Griffiths, W. C. Kong, S. A. Richards, G. A. Burley, M. C. Willis, E. P. A. Talbot, *Chem. Sci.*, **2018**, *9*, 2295-2300.

[19] a) C. Zhang, Y. Chen, G. Yuan, *Chin. J. Chem.* **2016**, *34*, 1277-1282; b) Y. Jiang, Q.-Q. Wang, S. Liang, L.-M. Hu, R. D. Little, C.-C. Zeng, *J. Org. Chem*. **2016**, *81*, 4713-4719; c) A. O. Terent'ev, O. M. Mulina, D. A. Pirgach, M. A. Syroeshkin, A. P. Glinushkin, G. I. Nikishin, *Mendeleev Commun*. **2016**, *26*, 538-539.

[20] a) Y. Fu, Y. Su, Q. Xu, Z. Du, Y. Hu, K.-H. Wang, D. Huang, *RSC Adv.* **2017**, *7*, 6018-6022; b) Y. Fu, W. Zhu, X. Zhao, H. Hügel, Z. Wu, Y. Su, Z. Du, D. Huang, Y. Hu, *Org. Biomol. Chem.* **2014**, *12*, 4295-4299; c) Y. Fu, X. Zhao, B. Hou, *Chin. J. Org. Chem.* **2016**, *36*, 1184-1196; d) Y. Fu, Q.-S. Xu, C.-Z. Shi, C.-Q. Xiao, Z. Du, *Adv. Synth. Catal.* **2018**, *360*, 3502-3506.

[21] a) C. Liu, Q. Lu, Z. Huang, J. Zhang, F. Liao, P. Peng, A. Lei, *Org. Lett.* **2015**, *17*, 6034-6037; b) X. Zhao, A. Wei, B. Yang, T. Li, Q. Li, D. Qiu, K. Lu, *J. Org. Chem*. **2017**, *82*, 9175-9181.

[22] The existence of molecular iodine was verified by the positive result of iodine-starch test.

[23] a) C. A. Giza, R. L. Hinmam, *J. Og .Chem*. **1964**, *29*, 1453-1461; b) P. L. Southwick, D. R. Christman, *J. Am. Chem. Soc.* **1952**, *74*, 1886-1891; c) L. C. R. M. da Frota, R. C. P. Canavez, S. L. da Silva Gomes, Paulo R. R. Costa, A.J. M. da Silva, *J. Braz. Chem. Soc*. **2009**, *20*, 1916-1920.

[24] 1,2-Dihaloethanes are prone to proceed halogen exchange reactions, see: L. Friederich, J. R. Duncan, G. L. Heard, D. W. Setser, B. E. Holmes, *J. Phys. Chem. A* **2010**, *114*, 4138-4147.

[25] a) P. Katrun, C. Mueanglaew, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorakram, C. Kuhakarn, *J. Org. Chem*. **2014**, *79*, 1778-1785; b) W. E. Truce, G. C. Wolf, *J. Org. Chem.* **1971**, *36*, 1727-1732.

[26] R. Konaka, K. Kuruma, S. Terabe, *J. Am. Chem. Soc*., **1968**, *90*, 1801-1806.

[27] a) P. L. Southwick, D. R. Christman, *J. Am .Chem. Soc.* **1952**, *74* 1886-1891; b) L. C. R. M. da Frota, R. C. P. Canavez, S. L. da Silva Gomes, P. R. R. Costa, A. J. M. da Silva, *J. Braz. Chem. Soc*., **2009**, *20*, 1916-1920.

[28] T. Hou, C. Zhang, Y. Wang, Z. Liu, Z. Zhang, F. Wang, *Cat. Commun*. **2017**, *94*, 56-59.

[29] a) T. S. Calderwood, D. T. Sawyer, *J. Am. Chem. Soc.* **1984**, *106*, 7185-7186; b) C. J. Christiansen, J. S. Francisco, *J. Phys. Chem. A* **2009**, *113*, 7189-7204.

…

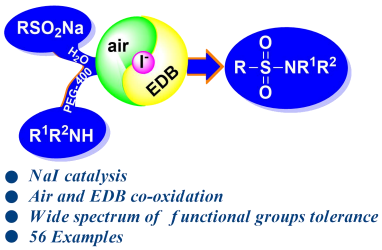
10.1002/ejoc.201801386

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION

A novel NaI-catalyzed oxidative amination of sodium sulfinates, employing both ethylene dibromide (EDB) and air as the oxidants, is described.



EDB/Air Co-OXIDATION

Ying Fu, Quan-Zhou Li, Qin-Shan Xu, Helmut Hügel, Ming-Peng Li and Zhengyin Du*

Page No. – Page No.

NaI-Catalyzed Oxidative Amination of Aromatic Sodium Sulfinates: Synergetic Effect of Ethylene