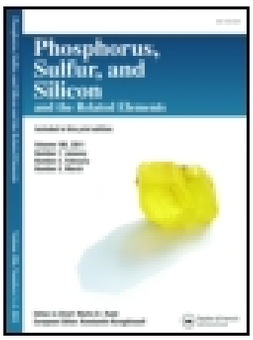


Taylor & Francis
Taylor & Francis Group

Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: https://www.tandfonline.com/loi/gpss20

Synthesis of sulfonamides promoted by alkyl iodide via a hypervalent iodine intermediate

Zhongshi Zhou & Xuehan He

To cite this article: Zhongshi Zhou & Xuehan He (2019): Synthesis of sulfonamides promoted by alkyl iodide via a hypervalent iodine intermediate, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2019.1686378

To link to this article: https://doi.org/10.1080/10426507.2019.1686378

PHOSPHORUS, SULFUR, AND SILICON AND THE RELATED ELEMENTS
https://doi.org/10.1080/10426507.2019.1686378

Synthesis of sulfonamides promoted by alkyl iodide via a hypervalent iodine intermediate

Zhongshi Zhou[a] and Xuehan He[b]

[a]College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou, People's Republic of China; [b]Zhejiang Institute of Geology and Mineral Resource, Hangzhou, People's Republic of China

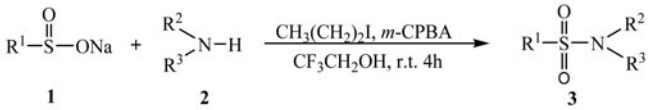
ABSTRACT

A new method for the preparation of sulfonamides from sodium sulfinates and amines is developed. A stoichiometric amount of *m*-chloroperbenzoic acid as oxidant and a catalytic amount of 1-iodopropane provides the corresponding sulfonamides in good yields under mild reaction conditions. In this protocol, 1-iodopropane is first oxidized by *m*-chloroperbenzoic acid into the corresponding hypervalent iodine intermediate iodosylpropane, which is highly unstable and decomposes at once to form hypoiodous acid. Then, the following reaction of the generated active hypoiodous acid with sodium sulfinates and amines results in the corresponding sulfonamides.

ARTICLE HISTORY
Received 21 August 2019
Accepted 15 October 2019

KEYWORDS
Sulfonamide; 1-iodopropane; sodium sulfinate; amine; synthesis

GRAPHICAL ABSTRACT



1 2 3

Introduction

Hypervalent iodine reagents have found broad application in organic chemistry and are nowadays frequently used in synthesis as they are nonmetallic oxidation reagents and avoid the issues of toxicity of many transition metals commonly involved in such processes.[1–7] In recent years, the catalytic utilization of hypervalent iodine reagents has been increasing in importance, with growing interest in the development of environmentally benign synthetic transformations.[8–13] In these catalytic reactions, a catalytic amount of an iodoarene together with a stoichiometric oxidant is used, which considerably decreases the need for expensive hypervalent iodine reagents. However, the use of an alkyl iodide in place of an iodoarene as catalyst in such reactions has much less been applied.[14–16] Therefore, research to extend alkyl substituted hypervalent iodine reagent applications in organic synthesis, especially in catalytic reactions, is still desired.

Sulfonamides are a privileged class of sulfur-containing compounds, and have found various clinical applications in medicine, including the use as antibacterials, diuretics, anticonvulsants, and HIV protease inhibitors.[17–23] The classic method for the synthesis of sulfonamides involves the reaction between an amine and a sulfonyl chloride, in the presence of a base.[24,25] However, this method has some limitations such as the use of hazardous starting materials and harsh reaction conditions. Recently, oxidative coupling reactions as alternative methods for obtaining sulfonamides have been reported.[26–30] This is interesting because readily available sodium sulfinates and amines are used as starting materials and the method is general and efficient. Very recently, Marques's group just developed a novel and convenient protocol for sulfonamide synthesis with 1-chloro-1,2-benziodoxol-3-(*1H*)-one in the presence of a hypervalent iodine reagent as the oxidant.[31] Since this is the first example of a hypervalent iodine reagent mediated sulfonamide synthesis, and in order to enrich and extend the scope of this method, we have investigated a novel oxidative coupling reaction promoted by a catalytic amount of alkyl iodide. Herein, we wish to report a new procedure for obtaining sulfonamides from sodium sulfinates and amines, which is promoted by 1-iodopropane combined with the oxidant *m*-chloroperbenzoic acid (*m*CPBA). To the best of our knowledge, this method has not been reported before.

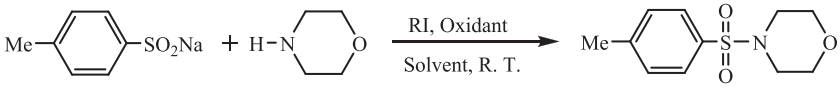
Results and discussion

In our recent research, we found that the spirocyclization of phenols can be carried out smoothly and efficiently with good yields under mild conditions with a catalytic amount of 1-iodopropane and a stoichiometric oxidant *m*CPBA.[16] On this basis, we first explored the reaction of sodium *p*-toluenesulfinate (**1a**) with morpholine (**2a**) in the presence of a

CONTACT Zhongshi Zhou zhoushan63@163.com College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou 310015, People's Republic of China.

Supplemental data for this article can be accessed here.

Table 1. Optimization of the reaction conditions for the synthesis of sulfonamides.



1a **2a** **3a**

Entry	*m*CPBA (equiv.)	RI (mol%)	Solvent	Time (h)	Yield (%)[a]
1	1.5	$CH_3(CH_2)_2I$ (10)	MeCN	10	34
2	1.5	–	MeCN	10	0
3	–	$CH_3(CH_2)_2I$ (10)	MeCN	10	0
4	1.5	$CH_3(CH_2)_2I$ (10)	CH_2Cl_2	10	12
5	1.5	$CH_3(CH_2)_2I$ (10)	DMF	10	8
6	1.5	$CH_3(CH_2)_2I$ (10)	EtOAc	10	25
7	1.5	$CH_3(CH_2)_2I$ (10)	CH_3OH	10	37
8	1.5	$CH_3(CH_2)_2I$ (10)	CF_3CH_2OH	10	52
9	1.5	$CH_3(CH_2)_2I$ (15)	CF_3CH_2OH	10	66
10	1.5	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	10	78
11	1.5	$CH_3(CH_2)_2I$ (30)	CF_3CH_2OH	10	80
12	1.5	$CH_3(CH_2)_2I$ (50)	CF_3CH_2OH	10	81
13	1.5	$CH_3(CH_2)_3I$ (20)	CF_3CH_2OH	10	62
14	1.5	$CH_3(CH_2)_4I$ (20)	CF_3CH_2OH	10	54
15	1.5	$CH_3(CH_2)_5I$ (20)	CF_3CH_2OH	10	47
16	1.5	CH_3CHICH_3 (20)	CF_3CH_2OH	10	51
17	1.5	CF_3CH_2I (20)	CF_3CH_2OH	10	38
18	1.0	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	10	56
19	2.0	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	10	77
20	2.5	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	10	59
21	Oxone® (1.5)	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	10	41
22	TBHP (1.5)	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	10	35
23	H_2O_2 (1.5)	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	10	61
24	1.5	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	6	78
25	1.5	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	4	81
26	1.5	$CH_3(CH_2)_2I$ (20)	CF_3CH_2OH	2	66

[a]Isolated yield.

catalytic amount of 1-iodopropane and a stoichiometric amount of *m*CPBA at room temperature. We observed that on stirring the mixture of 1.0 equiv. of **1a**, 1.5 equiv. of **2a**, and *m*CPBA with 10 mol% 1-iodopropane in MeCN for 10 h the expected product 4-[(4-methylphenyl)sulfonyl]morpholine (**3a**) was obtained in 34% yield (Table 1, entry 1). In the light of the successful formation of **3a**, the reaction conditions were then optimized (Table 1). In the control experiments, **3a** was not formed in the absence of 1-iodopropane or *m*CPBA (Table 1, entries 2 and 3). After screening several solvents, CF_3CH_2OH was found to be a suitable solvent for the reaction (entries 1 and 4–8). In CF_3CH_2OH, the optimal amount of 1-iodopropane was determined and 20 mol% proved to be the best choice (entries 8–12). Other alkyl iodides can also promote the reaction. However, they resulted in low yields of **3a** compared with 1-iodopropane (entries 10 and 13–17). Of several oxidants, *m*CPBA was the most effective one and its suitable amount was 1.5 equiv. (entries 10 and 18–23). Under the optimized conditions, the reaction proceeded smoothly and was completed in 4 h (entries 10 and 24–26).

Based on the extensive screening process, we arrived at the optimal reaction conditions. The oxidative coupling reaction of 1.0 equiv. of sodium sulfinates (**1**) with 1.5 equiv. of amines (**2**) and *m*CPBA, as well as 20 mol% of $CH_3(CH_2)_2I$ in CF_3CH_2OH proceeded smoothly at room temperature for 4 h, and a series of corresponding sulfonamides (**3**) were obtained. The results are summarized in Table 2.

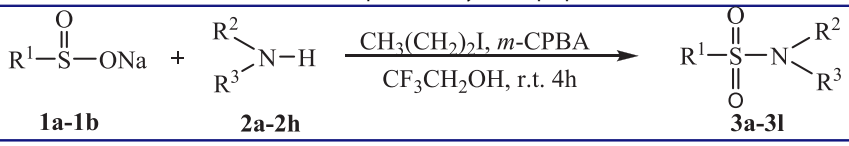
As shown in Table 2, the reaction was compatible with most of the studied primary and secondary amines when two sodium sulfinates were treated, which provided the corresponding products **3** in good yields (Table 2, entries 1–6 and 9–12). The yield decreased to 51% when an allylamine (**2g**) was used. This is mainly due to the double bond which is sensitive to the oxidant *m*CPBA (entry 7). Similarly, aniline (**2h**) was easier oxidized compared with other aliphatic amines, which resulted in a poor yield (entry 8).

According to the above results, a plausible reaction pathway is proposed in Scheme 1. Thus, 1-iodopentane is first oxidized by *m*CPBA into the corresponding hypervalent iodine intermediate iodosylpropane, which is highly unstable and decomposes at once to form hypoiodous acid.[14] Then, the following reaction of the active hypoiodous acid with sodium sulfinate results in the active sulfonyl iodide, which is immediately attacked by the nucleophilic amine to yield the desired product sulfonamide. The reduced by-product HI is re-oxidized into the hypoiodous acid by *m*CPBA to complete the recycling reaction. To corroborate the above mechanism, we used a stoichiometric amount of hypoiodous acid to treat **1a** and **2a** in CF_3CH_2OH. A 55% yield of product **3a** was obtained. Finally, a stoichiometric amount of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), was added to the reaction mixture of **1a**, **2a**, *m*CPBA, and I_2 under the optimized conditions. It was found that the reaction occurred still very well, indicating that the reaction may not undergo a radical pathway.

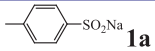
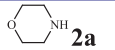
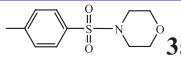
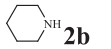
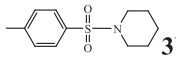
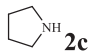
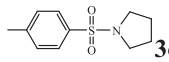
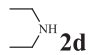
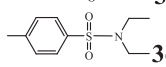
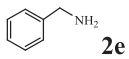
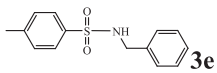
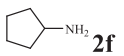
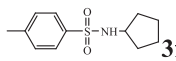
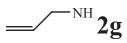
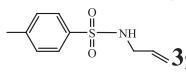
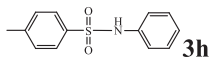
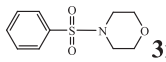
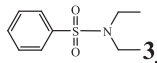
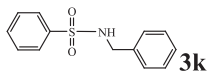
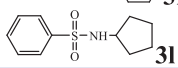
Conclusions

We have developed a new and convenient procedure for the synthesis of sulfonamides from sodium sulfinates, amines,

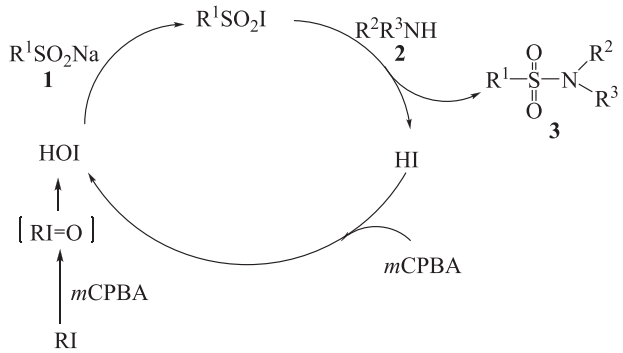
Table 2. Preparation of sulfonamides from sodium sulfinates and amines promoted by 1-iodopropane.



1a-1b **2a-2h** **3a-3l**

Entry	Sodium sulfinates **1**	Amines **2**	Products **3**	Yield (%)[a]
1	 **1a**	 **2a**	 **3a**	81
2	**1a**	 **2b**	 **3b**	77
3	**1a**	 **2c**	 **3c**	80
4	**1a**	 **2d**	 **3d**	71
5	**1a**	 **2e**	 **3e**	75
6	**1a**	 **2f**	 **3f**	68
7	**1a**	 **2g**	 **3g**	51
8	**1a**	$PhNH_2$ **2h**	 **3h**	30
9	$PhSO_2Na$ **1b**	**2a**	 **3i**	78
10	**1b**	**2d**	 **3j**	67
11	**1b**	**2e**	 **3k**	73
12	**1b**	**2f**	 **3l**	66

[a]Isolated yields.



Scheme 1. Proposed mechanism for the synthesis of sulfonamides promoted by alkyl iodide.

and *m*CPBA in the presence of catalytic amounts of 1-iodopropane at room temperature. This method has some advantages such as mild reaction conditions, simple procedure, and affording a series of sulfonamides mostly with good yields. Furthermore, the use of alkyl iodide in the sulfonamide synthesis will extend the scope of alkyl substituted hypervalent iodine reagents in organic synthesis.

Experimental section

General

IR spectra were recorded on a Thermo-Nicolet 6700 instrument; ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker-AVANCE III (500 MHz) spectrometer; Mass spectra were determined on Waters-GCT Premier, Thermo-DECAX-60000 LCQ Deca XP and Thermo-ITQ 1100 mass spectrometers. Sodium sulfinates, amines, alkyl iodides, *m*CPBA, and solvents were commercially available. The Supplemental Materials contains sample ^{1}H and ^{13}C NMR spectra for the known products 3 (Figures S1–S10).

General procedure for the synthesis of sulfonamides

Sodium sulfinates **1** (1.0 mmol), amines **2** (1.5 mmol), 1-iodopropane (0.2 mmol), and *m*CPBA (1.5 mmol) were added successively into CF_3CH_2OH (5.0 mL). The suspension mixture was vigorously stirred at room temperature for 4 h. Upon completion, the reaction mixture was quenched by addition of sat. aq. $Na_2S_2O_3$ (3 mL), sat. aq. Na_2CO_3 (8 mL) and H_2O (10 mL), respectively. The mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified on a silica gel plate (3:1 petroleum ether-ethyl acetate) to furnish the products **3**.

4-[(4-Methylphenyl)sulfonyl]morpholine 3a

White solid.[31] IR (KBr): 2853, 1453, 1346, 1165, 1114, 941, 815, 734, 545 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm):

7.63 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 3.73 (t, $J = 4.7$ Hz, 4H), 2.98 (t, $J = 4.7$ Hz, 4H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.9, 132.1, 129.7, 127.9, 66.1, 45.9, 21.6. MS (ESI): *m/z* (%) 242 (M + 1).

1-[(4-Methylphenyl)sulfonyl]piperidine 3b

White solid.[31] IR (KBr): 2929, 2831, 1453, 1338, 1168, 1093, 932, 813, 725, 550 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.61 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 2.93 (t, $J = 5.5$ Hz, 4H), 2.41 (s, 3H), 1.66–1.53 (m, 4H), 1.41–1.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.2, 133.0, 129.4, 127.4, 46.8, 25.0, 23.3, 21.2. MS (ESI): *m/z* (%) 240 (M + 1).

1-[(4-Methylphenyl)sulfonyl]pyrrolidine 3c

White solid.[27] IR (KBr): 2983, 1466, 1331, 1154, 816, 695, 549 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.70 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 3.20 (t, $J = 6.8$ Hz, 4H), 2.42(s, 3H), 1.76–1.70 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.5, 134.0, 129.8, 127.9, 48.1, 25.5, 21.7. MS (ESI): *m/z* (%) 248 (M + 23).

N,N-Diethyl-4-methylbenzenesulfonamide 3d

Pale yellow solid.[30] IR (KBr): 2978, 2930, 1464, 1330, 1154, 815, 697, 548 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.68 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 3.23 (t, $J = 7.2$ Hz, 4H), 2.40 (s, 3 H), 1.12 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 142.9, 137.5, 129.5, 127.2, 42.0, 21.5, 14.0. MS (ESI): *m/z* (%) 228 (M + 1).

N-Benzyl-4-methylbenzenesulfonamide 3e

White solid.[30] IR (KBr): 3270, 1456, 1325, 1168, 1066, 875, 746, 684, 552 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.76 (d, $J = 8.3$ Hz, 2H), 7.33–7.23 (m, 5H), 7.24–7.20 (m, 2H), 4.95 (d, $J = 5.3$ Hz, 1H), 4.12 (d, $J = 6.2$ Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.5, 136.8, 136.2, 129.7, 128.6, 127.9, 127.8, 127.4, 47.2, 21.6. MS (ESI): *m/z* (%) 279 (M + 17).

N-Cyclopentyl-4-methylbenzenesulfonamide 3f

Pale yellow solid.[30] IR (KBr): 3255, 2966, 2868, 1326, 1159, 1090, 813, 688, 566 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.78 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 5.28 (d, $J = 7.2$ Hz, 1H), 3.54 (dd, $J = 13.6$, 6.8 Hz, 1H), 2.42 (s, 3H), 1.76–1.69 (m, 2H), 1.62–1.55 (m, 2H), 1.47–1.30 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.0, 137.8, 129.6, 127.1, 55.0, 33.2, 23.0, 21.5. MS (ESI): *m/z* (%) 240 (M + 1).

N-Allyl-4-methylbenzenesulfonamide 3g

White solid.[27] ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.76 (d, $J = 7.8$ Hz, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 5.73 (ddt, $J = 16.4$, 10.8, 5.6 Hz, 1H), 5.13 (dd, $J = 18.2$, 13.6 Hz, 2H), 4.62 (s, 1H), 3.60 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.6, 137.0, 133.1, 129.9, 127.2, 117.8, 45.8, 21.8. MS (ESI): *m/z* (%) 212 (M + 1).

4-Methyl-N-phenylbenzenesulfonamide 3h

White solid.[27] ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.93–7.55 (m, 3H), 7.44–6.88 (m, 7H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.8, 136.8, 136.1, 129.6, 129.2, 127.3, 125.0, 121.3, 21.5. MS (ESI): *m/z* (%) 248 (M + 1).

4-(Phenylsulfonyl)morpholine 3i

White solid.[29] IR (KBr): 2988, 1459, 1347, 1260, 1168, 1109, 949, 746, 693, 532 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.79–7.72 (m, 2H), 7.66–7.62 (m, 1H), 7.60–7.52 (m, 2H), 3.73 (t, $J = 4.8$ Hz, 4H), 3.00 (t, $J = 4.8$ Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 135.0, 133.0, 129.1, 127.9, 66.0, 45.8. MS (ESI): *m/z* (%) 228 (M + 1).

N,N-Diethylbenzenesulfonamide 3j

Colorless viscous oil.[27] IR (KBr): 2988, 1449, 1333, 1157, 1020, 732, 692, 579 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.82–7.75 (m, 2H), 7.57–7.51 (m, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 3.23 (q, $J = 7.2$ Hz, 4H), 1.11 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 140.3, 132.2, 129.0, 126.8, 42.1, 14.0. MS (ESI): *m/z* (%) 214 (M + 1).

N-Benzylbenzenesulfonamide 3k

White solid.[29] IR (KBr): 3334, 1328, 1162, 1098, 1061, 750, 688 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.86 (d, $J = 7.2$ Hz, 2H), 7.59–7.52 (m, 1H), 7.50–7.43 (m, 2H), 7.27–7.20 (m, 3H), 7.20–7.16 (m, 2H), 5.43 (t, $J = 6.2$ Hz, 1H), 4.12 (d, $J = 6.3$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 139.9, 136.2, 132.6, 129.0, 128.5, 127.8, 127.6, 126.8, 47.0. MS (ESI): *m/z* (%) 265 (M + 17).

N-Cyclopentylbenzenesulfonamide 3l

Pale yellow solid.[26] IR (KBr): 3234, 2978, 1448, 1319, 1152, 1092, 722, 687, 592, 555 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.93–7.87 (m, 2H), 7.61–7.54 (m, 1H), 7.54–7.48 (m, 2H), 5.08 (d, $J = 7.2$ Hz, 1H), 3.59 (dd, $J = 13.8$, 6.8 Hz, 1H), 1.80–1.70 (m, 2H), 1.64–1.56 (m, 2H), 1.50–1.28 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 140.9, 132.4, 129.2, 127.0, 55.1, 33.3, 23.2. MS (ESI): *m/z* (%) 226 (M + 1).

References

[1] Varvoglis, A. Chemical Transformations Induced by Hypervalent Iodine Reagents. *Tetrahedron* **1997**, *53*, 1179–1255. DOI: 10.1016/S0040-4020(96)00970-2.

[2] Stang, P. J.; Zhdankin, V. V. Organic Polyvalent Iodine Compounds. *Chem. Rev.* **1996**, *96*, 1123–1178. DOI: 10.1021/cr940424+.

[3] Zhdankin, V. V.; Stang, P. J. Recent Developments in the Chemistry of Polyvalent Iodine Compounds. *Chem. Rev.* **2002**, *102*, 2523–2584. DOI: 10.1021/cr010003+.

[4] Zhdankin, V. V.; Stang, P. J. Chemistry of Polyvalent Iodine. *Chem. Rev.* **2008**, *108*, 5299–5358. DOI: 10.1021/cr800332c.

[5] Kirschning, A. Hypervalent Iodine and Carbohydrates—A New Liaison. *Eur. J. Org. Chem.* **1998**, *11*, 2267–2274. DOI: 10.1002/(SICI)1099-0690(199811)1998:11 < 2267::AID-EJOC2267 > 3.0.CO;2-E.

[6] Okuyama, T. Solvolysis of Vinyl Iodonium Salts. New Insights into Vinyl Cation Intermediates. *Acc. Chem. Res.* **2002**, *35*, 12–18. DOI: 10.1021/ar0100374.

[7] Grushin, V. V. Cyclic Diaryliodonium Ions: Old Mysteries Solved and New Applications Envisaged. *Chem. Soc. Rev.* **2000**, *29*, 315–324. DOI: 10.1039/a909041j.

[8] Ochiai, M.; Takeuchi, Y.; Katayama, T.; Sueda, T.; Miyamoto, K. Iodobenzene-Catalyzed α-Acetoxylation of Ketones. In Situ Generation of Hypervalent (Diacyloxyiodo)Benzenes Using *m*-Chloroperbenzoic Acid. *J. Am. Chem. Soc.* **2005**, *127*, 12244–12245. DOI: 10.1021/ja0542800.

[9] Richardson, R. D.; Wirth, T. Hypervalent Iodine Goes Catalytic. *Angew. Chem. Int. Ed.* **2006**, *45*, 4402–4404. DOI: 10.1002/anie.200601817.

[10] Dohi, T.; Kita, Y. Hypervalent Iodine Reagents as a New Entrance to Organocatalysts. *Chem. Commun.* **2009**, 2073–2085. DOI: 10.1039/B821747E.

[11] Uyanik, M.; Ishihara, K. Hypervalent Iodine-Mediated Oxidation of Alcohols. *Chem. Commun.* **2009**, 2086–2099. DOI: 10.1039/B823399C.

[12] Zhou, Z. S.; He, X. H. An Efficient and Regioselective Monobromination of Electron-Rich Aromatic Compounds Using Catalytic Hypervalent Iodine(III) Reagent. *Synthesis* **2011**, 207–209. DOI: 10.1055/s-0030-1258350.

[13] Dohi, T.; Minamitsuji, Y.; Maruyama, A.; Hirose, S.; Kita, Y. A New H_2O_2/Acid Anhydride System for the Iodoarene-Catalyzed C − C Bond-Forming Reactions of Phenols. *Org. Lett.* **2008**, *10*, 3559–3562. DOI: 10.1021/ol801321f.

[14] Asensio, G.; Andreu, C.; Boix-Bernardini, C.; Mello, R.; Gonzalez-Nunez, M. E. Iodomethane Oxidation by Dimethyldioxirane: A New Route to Hypoiodous Acid and Iodohydrines. *Org. Lett.* **1999**, *1*, 2125–2128. DOI: 10.1021/ol9903281.

[15] Zhang, B. J.; Han, L. Q.; Hu, J. T.; Yan, J. Novel α-Tosyloxylation of Ketones Catalyzed by the *In Situ* Generated Hypoiodous Acid from Alkyl Iodide. *Tetrahedron Lett.* **2014**, *55*, 5851–5854. DOI: 10.1016/j.tetlet.2014.08.093.

[16] Zhou, Z. S.; He, X. H. Convenient Catalysed Spirocyclisation of 4-(2-Carboxyethyl)Phenols. *J. Chem. Res.* **2017**, *41*, 57–59. DOI: 10.3184/174751917X14840718425897.

[17] Supuran, C. T.; Casini, A.; Scozzafava, A. Protease Inhibitors of the Sulfonamide Type: Anticancer, anti-Inflammatory, and Antiviral Agents. *Med. Res. Rev.* **2003**, *23*, 535–558. DOI: 10.1002/med.10047.

[18] Huang, Z.; Lin, Z.; Huang, J. A Novel Kind of Antitumour Drugs Using Sulfonamide as Parent Compound. *Eur. J. Med. Chem.* **2001**, *36*, 863–872. DOI: 10.1016/S0223-5234(01)01285-5.

[19] Winum, J. Y.; Scozzafava, A.; Montero, J. L.; Supuran, C. T. Therapeutic Potential of Sulfamides as Enzyme Inhibitors. *Med. Res. Rev.* **2006**, *26*, 767–792. DOI: 10.1002/med.20068.

[20] Chohan, Z. H.; Youssoufi, M. H.; Jarrahpour, A.; Hadda, T. B. Identification of Antibacterial and Antifungal Pharmacophore Sites for Potent Bacteria and Fungi Inhibition: Indolenyl Sulfonamide Derivatives. *Eur. J. Med. Chem.* **2010**, *45*, 1189–1199. DOI: 10.1016/j.ejmech.2009.11.029.

[21] Chandrasekhar, S.; Mohapatra, S. Neighbouring Group Assisted Sulfonamide Cleavage of Sharpless Aminols under Acetonation Conditions. *Tetrahedron Lett.* **1998**, *39*, 695–698. DOI: 10.1016/S0040-4039(97)10638-4.

[22] Scozzafava, A.; Owa, T.; Mastrolorenzo, A.; Supuran, C. T. Anticancer and Antiviral Sulfonamides. *Curr. Med. Chem.* **2003**, *10*, 925–953. DOI: 10.2174/0929867033457647.

[23] Bano, S.; Javed, K.; Ahmad, S.; Rathish, I. G.; Singh, S.; Alam, M. S. Synthesis and Biological Evaluation of Some New 2-Pyrazolines Bearing Benzene Sulfonamide Moiety as Potential Anti-Inflammatory and Anti-Cancer Agents. *Eur. J. Med. Chem.* **2011**, *46*, 5763–5768. DOI: 10.1016/j.ejmech.2011.08.015.

[24] Andersen, K. *In Comprehensive Organic Chemistry*; Pergamon Press: Oxford, **1979**; Vol. 3.

[25] Harmata, M.; Zheng, P.; Huang, C.; Gomes, M. G.; Ying, W.; Ranyanil, K.-O.; Balan, G.; Calkins, N. L. Expedient Synthesis of Sulfinamides from Sulfonyl Chlorides. *J. Org. Chem.* **2007**, *72*, 683–685. DOI: 10.1021/jo062296i.

[26] Yang, K.; Ke, M.; Lin, Y.-G.; Song, Q.-L. Sulfonamide Formation from Sodium Sulfinates and Amines or Ammonia under Metal-Free Conditions at Ambient Temperature. *Green Chem.* **2015**, *17*, 1395–1399. DOI: 10.1039/C4GC02236J.

[27] Wei, W.; Liu, C.-L.; Yang, D.-S.; Wen, J.-W.; You, J.-M.; Wang, H. Metal-Free Direct Construction of Sulfonamides via Iodine-Mediated Coupling Reaction of Sodium Sulfinates and Amines at Room Temperature. *Adv. Synth. Catal.* **2015**, *357*, 987–992. DOI: 10.1002/adsc.201400801.

[28] Zhao, J.-W.; Xu, J.-X.; Chen, J.-X.; Wang, X.-Q.; He, M.-H. Metal-Free Oxidative Coupling of Amines with Sodium Sulfinates: A Mild Access to Sulfonamides. *RSC Adv.* **2014**, *4*, 64698–64701. DOI: 10.1039/C4RA13454K.

[29] Chonchanok, B.; Danupat, B.; Sirilata, Y. Iodine-Catalyzed Oxidative Amination of Sodium Sulfinates: A Convenient Approach to the Synthesis of Sulfonamides under Mild Conditions. *Eur. J. Org. Chem.* **2015**, 1575–1582. DOI: 10.1002/ejoc.201403531.

[30] Wu, S. X.; Zhang, Y. K.; Zhu, M.; Yan, J. One-Pot Synthesis of Sulfonamides from Sodium Sulfinates and Amines via Sulfonyl Bromides. *Synlett* **2016**, *27*, 2699–2704. DOI: 10.1055/s-0036-1588298.

[31] Poeira, D. L.; Macara, J.; Faustino, H.; Coelho, J. A. S.; Gois, P. M. P.; Marques, M. M. B. Hypervalent Iodine Mediated Sulfonamide Synthesis. *Eur. J. Org. Chem.* **2019**, 2695–2701. DOI: 10.1002/ejoc.201900259.