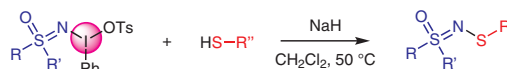


Electrophilic Sulfoximidations of Thiols by Hypervalent Iodine Reagents

Han Wang
Duo Zhang
Mengwei Cao
Carsten Bolm*

Institute of Organic Chemistry, RWTH Aachen University,
Landoltweg 1, 52074 Aachen, Germany
Carsten.bolm@rwth-aachen.de



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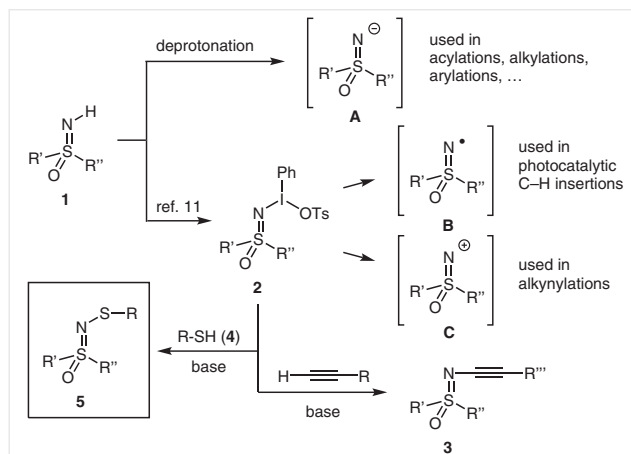
Abstract A new electrophilic sulfoximidation of thiols has been developed. Using sodium hydride as a base, the treatment of sulfoximidoyl-containing hypervalent iodine(III) reagents with thiols affords the corresponding *N*-sulfonylsulfoximines (*N*-thiosulfoximines) in good to excellent yields. A plausible mechanism is proposed.

Key words sulfoximidation, thiol, *N*-sulfonylsulfoximine, hypervalent iodine reagents, ligand exchange

Sulfoximines are monoaza analogues of sulfones with relevance for asymmetric synthesis¹ and applications in crop protection and medicinal chemistry.² They exhibit manifold reaction behavior, as reflected by Trost and Matsuoaka, who described *N*-nitrosulfoximines as ‘chemical chameleons’.³ In general, substituents at the sulfoximidoyl group affect the properties of the respective molecules,^{4,5} allowing, for example, fine-tuning of important parameters such as pK_a ⁶ and solubility.⁷ The *N*-substituent plays a key role in this context. Besides introducing it directly by sulfide or sulfoxide imidation,^{4,8} it can be varied by functionalizing *NH*-sulfoximines **1**, which are readily accessible by various routes.^{1,9} Most protocols involve deprotonated intermediates **A**, which react with electrophiles to give acylated, alkylated, or arylated products among others.¹⁰ Alternative *N*-modification pathways via radicals **B** or cationic species **C** are rare.

In 2016 we introduced hypervalent iodine(III) compounds **2** with the vision to apply them synthetically as sulfoximidoyl transfer agents (Scheme 1).^{11,12} To our delight, photocatalysis allowed activation of the central I–N bond of **2** leading to functionalizations of benzylic C–H

bonds by the resulting sulfoximidoyl moieties.^{10g,13} In terms of the mechanism, the process was suggested to proceed via radicals such as **B**. While searching for new applications of iodine reagents **2**, we began focusing on pathways via (formally) cationic species **C**. Until now, only one transformation reflecting such reactivity is known. In the respective reaction scheme, reagents **2** react with terminal alkynes in the presence of a base affording *N*-alkynylated sulfoximines **3**.¹¹ After screening a series of other nucleophiles, we have now also discovered that deprotonated thiols were capable of reacting with **2** leading to *N*-sulfonylsulfoximines with the general structure **5**. Products of type **5** were known, but the common synthetic procedures started from *NH*-sulfoximines **1**, which were either *N*-derivatized by deprotonation followed by treatment with electrophilic sulfur reagents (such as $ArSCl$)¹⁴ or coupled with preformed¹⁵ or thiol-derived disulfides^{16,17} under metal catalysis. Thus, our new approach contrasted all previous ones.



Scheme 1 General reaction behavior of *NH*-sulfoximines **1** and access to target compounds **5** via iodine reagents **2**

The initial studies were performed with *S*-methyl-*S*-phenyl derivative **2a** and thiophenol (**4a**) as representative substrates. In dichloroethane (DCE), both compounds did not react at ambient temperature or at 70 °C, and only the starting materials were recovered (Table 1, entries 1 and 2). Also the addition of DBU, K₂CO₃, or KO^t-Bu did not lead to a breakthrough, and at best, traces of the expected product **5aa** were observed (Table 1, entries 3–5). The situation changed, when NaH was applied as base, and after a short optimization of the reaction conditions (Table 1, entries 6–11), *N*-sulfonylsulfoximine **5aa** was obtained in 91% yield (Table 1, entry 11).

Table 1 Optimization of the Reaction Parameters^a

Entry	Base (equiv)	Solvent	Temp (°C)	Yield (%)
1	–	DCE	25	n.r.
2	–	DCE	70	n.r.
3	DBU (2.1)	DCE	25	trace
4	K ₂ CO ₃ (2.1)	DCE	25	n.d.
5	KO ^t -Bu (2.1)	DCE	25	trace
6	NaH (2.1)	DCE	25	27
7	NaH (2.1)	DCE	50	71
8	NaH (2.1)	MeCN	50	21
9	NaH (2.1)	THF	50	17
10	NaH (2.1)	CH ₂ Cl ₂	50	75
11 ^b	NaH (4.2)	CH ₂ Cl ₂	50	91

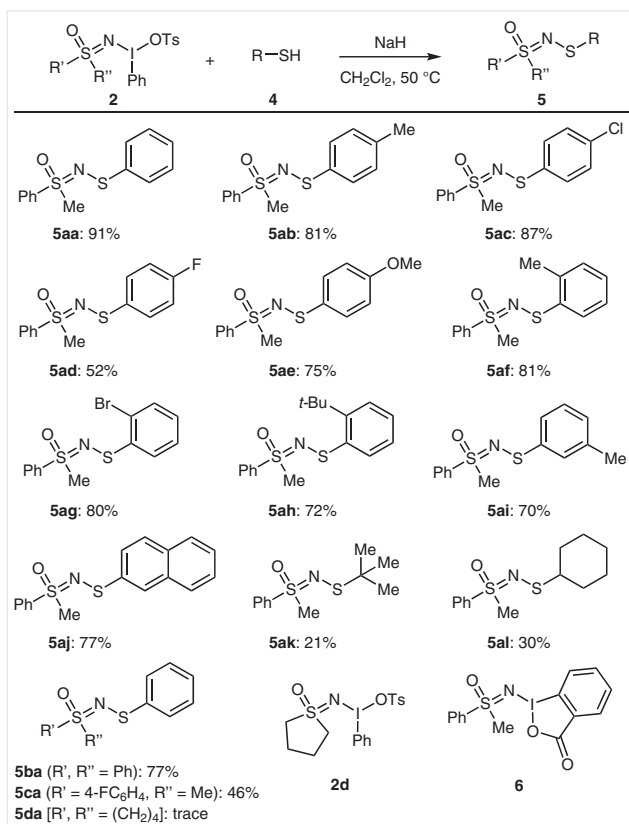
^a Reaction conditions (0.2-mmol scale): iodine reagent **2a**, thiophenol (**4a**; 2 equiv), base, solvent (2 mL), sealed tube, 16 h. n.r. = no reaction, n.d. = not detected.

^b Use of 4 equiv of **4a**.

To achieve this result, the following parameters were important: First, the ratio of starting materials **2a** and **4a** had to be 1:4. Second, the solvent needed to be dichloromethane, and third, the reaction temperature had to be 50 °C.

With the optimized conditions in hand, the substrate scope was examined. The results for reactions performed on a 0.2-mmol scale with respect to **2a** (in sealed tubes) are summarized in Scheme 2. First, various aromatic thiols were reacted with hypervalent iodine reagent **2a**. All products **5aa–aj** were obtained in good to high yields (52–91%). Electronic or steric effects induced by substituents on the thiophenol did not have an apparent impact on the reaction efficiency. Also *ortho*-substituted thiols reacted remarkably well as reflected by the results for products **5af–ah**, which were isolated in yields of 81%, 80%, and 72%, respectively. Reactions of **2a** with aliphatic thiols proved more difficult. Thus, **5ak** and **5al** stemming from couplings of **2a** with 2-

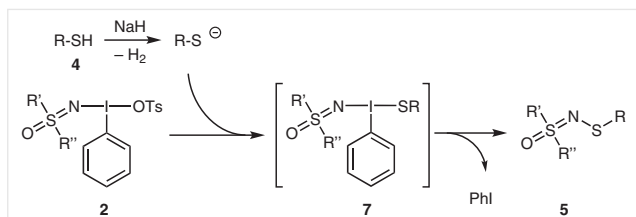
methylpropane-2-thiol (**4k**) and cyclohexanethiol (**4l**) were obtained in only 21% and 30%, respectively. Varying the structure of the hypervalent iodine reagent was possible too, and applying *S,S*-diphenyl and *S*-(4-fluorophenyl)-*S*-methyl derivatives **2b** and **2c** in reactions with thiophenol (**4a**) led to the corresponding products **5ba** and **5ca** in 77% and 46% yield, respectively. With tetrahydrothiophene derivative **2d** as the coupling agent for **4a**, only traces of the corresponding product **5da** were observed. The attempt to use 1-sulfoximidoyl-1,2-benziodoxole **6** in the reaction with **4a** remained unsuccessful.¹⁸



Scheme 2 Syntheses of *N*-sulfonylsulfoximines

Based on previous reports,^{11,19,20} we suggest the pathway depicted in Scheme 3 for the formation of *N*-sulfonylsulfoximines **5**. First, thiol **4** is deprotonated by sodium hydride, and the resulting thiolate reacts with hypervalent iodine reagent **2** by tosylate substitution. This ligand exchange leads to the formation of a transient intermediate **7**, which upon elimination of iodobenzene provides product **5**.

In summary, we developed a new approach towards *N*-sulfonylsulfoximines by electrophilic sulfoximidations of thiols with sulfoximidoyl-containing hypervalent iodine(III) reagents. Both *N*-(arylsulfonyl)- as well as *N*-(alkylsulfonyl)sulfoximines can easily be obtained under metal-free conditions.



Scheme 3 Possible reaction pathway

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Abcr, Acros, Sigma Aldrich, Merck) and used without further purification. When required, solvents were dried according to general purification methods. The product mixtures were analyzed by TLC using silica gel plates (Merck-Schuchardt) with fluorescent indicator ($\lambda = 254$ nm). The purification of the products was performed by flash column chromatography using silica gel 60 (63–200 μm) from Merck. NMR spectra were recorded on Agilent VNMRs 600, Agilent VNMRs 400 or Varian Mercury 300 in deuterated solvents. The IR spectra were recorded with a PerkinElmer Spectrum 100 spectrometer with an attached UATR device Diamond KRS-5; all IR data were collected by attenuated total reflectance (ATR). Mass spectra were recorded on a Finnigan SSQ Finnigan 7000 spectrometer (EI, 70 eV). HRMS were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer. Melting points (mp) were measured on a Büchi B-540 melting point apparatus.

N-Thiosulfoximines 5aa–da; General Procedure

Thiol **4** (0.80 mmol), NaH (0.80 mmol, 32 mg, wt = 60%), and CH_2Cl_2 (2.0 mL) were added to a flame-dried reaction tube (15 mL) equipped with a magnetic stirring bar, and the mixture was stirred at 50 °C for 4 h. Then, the hypervalent iodine(III) salt **2** (0.20 mmol) was added to the mixture in one portion. The resulting solution was stirred for 12 h at 50 °C and then cooled to r.t. Concentration under reduced pressure and subsequent purification of the product by column chromatography (silica gel, EtOAc/pentane 1:2) afforded *N*-thiosulfoximines **5**.

N-(Phenylthio)-S-methyl-S-phenylsulfoximine (5aa)¹⁵

Pale yellow viscous oil; yield: 48 mg (91%).

¹H NMR (600 MHz, CDCl_3): $\delta = 7.98$ – 7.94 (m, 2 H), 7.68 – 7.65 (m, 1 H), 7.60 – 7.56 (m, 2 H), 7.41 – 7.38 (m, 2 H), 7.27 – 7.25 (m, 2 H), 7.09 (t, $J = 7.3$ Hz, 1 H), 3.28 (s, 3 H).

¹³C{¹H} NMR (151 MHz, CDCl_3): $\delta = 142.1$, 138.7 , 133.7 , 129.5 , 128.5 , 128.4 , 125.1 , 123.8 , 43.8 .

N-(4-Methylphenylthio)-S-methyl-S-phenylsulfoximine (5ab)

Pale yellow viscous oil; yield: 45 mg (81%).

IR (ATR): 3476, 3309, 3018, 2922, 2325, 2015, 1907, 1735, 1487, 1217, 1091, 987, 804, 738, 686 cm^{-1} .

¹H NMR (600 MHz, CDCl_3): $\delta = 7.95$ – 7.93 (m, 2 H), 7.67 – 7.64 (m, 1 H), 7.59 – 7.56 (m, 2 H), 7.32 – 7.31 (d, $J = 6.0$ Hz, 2 H), 7.10 – 7.08 (m, 2 H), 3.26 (s, 3 H), 2.30 (s, 3 H).

¹³C{¹H} NMR (151 MHz, CDCl_3): $\delta = 138.8$, 138.2 , 135.3 , 133.6 , 129.4 , 129.3 , 128.4 , 125.0 , 43.7 , 21.0 .

MS (EI): $m/z = 277$ (13, M^+), 261 (4), 140 (23), 125 (21), 123 (100), 91 (22), 77 (72).

HRMS: m/z calcd for $[\text{C}_{14}\text{H}_{15}\text{NOS}_2 + \text{H}]^+$: 278.0668; found: 278.0668.

N-(4-Chlorophenylthio)-S-methyl-S-phenylsulfoximine (5ac)

Pale yellow oil; yield: 51 mg (87%).

IR (ATR): 3459, 3064, 2923, 2662, 2331, 2100, 1739, 1469, 1391, 1211, 1089, 981, 816, 735, 683 cm^{-1} .

¹H NMR (600 MHz, CDCl_3): $\delta = 7.94$ – 7.92 (m, 2 H), 7.69 – 7.66 (m, 1 H), 7.60 – 7.58 (m, 2 H), 7.33 – 7.31 (d, $J = 6.0$ Hz, 2 H), 7.23 – 7.21 (m, 2 H), 3.28 (s, 3 H).

¹³C{¹H} NMR (151 MHz, CDCl_3): $\delta = 140.9$, 138.5 , 133.9 , 130.6 , 129.6 , 128.6 , 128.4 , 125.1 , 43.9 .

MS (EI): $m/z = 298$ (95, M^+), 143 (88), 140 (48), 125 (84), 124 (100), 111 (21), 77 (81).

HRMS: m/z calcd for $[\text{C}_{13}\text{H}_{12}\text{ClNOS}_2 + \text{H}]^+$: 298.0122; found: 298.0122.

N-(4-Fluorophenylthio)-S-methyl-S-phenylsulfoximine (5ad)

Yellow oil; yield: 29 mg (52%).

IR (ATR): 3459, 3302, 3059, 2660, 2323, 2090, 1911, 1739, 1584, 1481, 1399, 1216, 1091, 986, 832, 741, 692 cm^{-1} .

¹H NMR (600 MHz, CDCl_3): $\delta = 7.94$ – 7.91 (m, 2 H), 7.69 – 7.65 (m, 1 H), 7.60 – 7.56 (m, 2 H), 7.41 – 7.37 (m, 2 H), 6.99 – 6.95 (m, 2 H), 3.27 (s, 3 H).

¹³C{¹H} NMR (101 MHz, CDCl_3): $\delta = 161.2$ (d, $J_{\text{C-F}} = 245.4$ Hz), 138.6 , 136.8 , 133.7 , 129.5 , 128.4 , 127.0 (d, $J_{\text{C-F}} = 8.1$ Hz), 115.6 (d, $J_{\text{C-F}} = 22.2$ Hz), 43.9 .

MS (EI): $m/z = 281$ (99, M^+), 141 (6), 140 (100), 127 (8), 125 (4), 124 (8), 95 (15), 77 (38).

HRMS: m/z calcd for $[\text{C}_{13}\text{H}_{12}\text{FNOS}_2 + \text{H}]^+$: 282.0417; found: 282.0420.

N-(4-Methoxyphenylthio)-S-methyl-S-phenylsulfoximine (5ae)

Yellow oil; yield: 44 mg (75%).

IR (ATR): 3460, 3298, 3062, 2929, 2667, 2328, 2096, 1906, 1730, 1586, 1487, 1226, 1091, 986, 825, 740, 686 cm^{-1} .

¹H NMR (600 MHz, CDCl_3): $\delta = 7.93$ – 7.91 (m, 2 H), 7.65 – 7.63 (m, 1 H), 7.58 – 7.56 (m, 2 H), 7.43 – 7.41 (m, 2 H), 6.84 – 6.82 (m, 2 H), 3.78 (s, 3 H), 3.23 (s, 3 H).

¹³C{¹H} NMR (101 MHz, CDCl_3): $\delta = 158.7$, 138.9 , 133.5 , 132.7 , 129.5 , 129.4 , 128.5 , 114.3 , 55.4 , 43.9 .

MS (EI): $m/z = 293$ (3, M^+), 154 (4), 140 (16), 139 (100), 125 (16), 124 (20), 107 (2), 77 (28).

HRMS: m/z calcd for $[\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}_2 + \text{H}]^+$: 294.0617; found: 294.0618.

N-(2-Methylphenylthio)-S-methyl-S-phenylsulfoximine (5af)

Pale yellow oil; yield: 45 mg (81%).

IR (ATR): 3458, 3302, 3055, 2924, 2665, 2326, 2103, 1905, 1738, 1584, 1452, 1212, 1092, 986, 738, 685 cm^{-1} .

¹H NMR (600 MHz, CDCl_3): $\delta = 7.97$ – 7.94 (m, 2 H), 7.66 – 7.62 (m, 1 H), 7.58 – 7.54 (m, 2 H), 7.31 – 7.27 (m, 1 H), 7.02 – 6.95 (m, 2 H), 3.27 (s, 3 H), 2.14 (s, 3 H).

¹³C{¹H} NMR (101 MHz, CDCl_3): $\delta = 140.7$, 138.8 , 133.6 , 132.1 , 129.4 , 129.4 , 128.4 , 126.2 , 124.5 , 123.3 , 43.8 , 18.8 .

MS (EI): $m/z = 277$ (91, M^+), 137 (20), 125 (29), 124 (44), 123 (14), 91 (14), 77 (31).

HRMS: m/z calcd for $[\text{C}_{14}\text{H}_{15}\text{NOS}_2 + \text{H}]^+$: 278.0668; found: 278.0670.

N-(2-Bromophenylthio)-S-methyl-S-phenylsulfoximine (5ag)

Yellow oil; yield: 55 mg (80%).

IR (ATR): 3458, 3058, 2926, 2669, 2325, 2097, 1915, 1738, 1570, 1438, 1316, 1211, 1092, 982, 912, 735 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 7.98–7.95 (m, 2 H), 7.67–7.65 (m, 2 H), 7.61–7.57 (m, 2 H), 7.36–7.32 (m, 2 H), 6.95–6.91 (m, 1 H), 3.31 (s, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 143.1, 138.6, 133.9, 131.8, 129.6, 128.3, 127.5, 125.5, 124.3, 115.9, 44.0.

MS (EI): m/z = 241 (25, M^+), 186 (2), 154 (2), 140 (12), 138 (2), 125 (45), 124 (100), 77 (18).

HRMS: m/z calcd for $[\text{C}_{13}\text{H}_{12}\text{BrONS}_2 + \text{Na}]^+$: 363.9436; found: 363.9440.

***N*-(2-*tert*-Butylphenylthio)-*S*-methyl-*S*-phenylsulfoximine (5ah)**

Pale yellow oil; yield: 46 mg (72%).

IR (ATR): 3456, 3058, 2960, 2328, 2094, 1911, 1738, 1583, 1446, 1313, 1211, 1092, 983, 741, 684 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 7.98–7.94 (m, 3 H), 7.64–7.62 (m, 1 H), 7.55–7.52 (m, 2 H), 7.26–7.22 (m, 1 H), 7.22–7.20 (m, 1 H), 7.06–7.03 (m, 1 H), 3.27 (s, 3 H), 1.32 (s, 9 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ = 144.8, 140.9, 138.9, 133.6, 129.3, 128.4, 126.1, 125.7, 125.6, 124.7, 43.7, 36.0, 29.9.

MS (EI): m/z = 319 (100, M^+), 165 (8), 140 (9), 133 (2), 125 (20), 124 (26), 77 (14).

HRMS: m/z calcd for $[\text{C}_{17}\text{H}_{21}\text{NOS}_2 + \text{K}]^+$: 358.0696; found: 358.0696.

***N*-(3-Methylphenylthio)-*S*-methyl-*S*-phenylsulfoximine (5ai)**

Colorless oil; yield: 39 mg (70%).

IR (ATR): 3427, 2905, 2655, 2321, 2096, 1920, 1730, 1627, 1583, 1446, 1322, 1244, 1147, 1089, 1000, 870, 746, 683 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 7.95–7.92 (m, 2 H), 7.66–7.62 (m, 1 H), 7.58–7.54 (m, 2 H), 7.20–7.12 (m, 3 H), 6.91–6.87 (m, 1 H), 3.26 (s, 3 H), 2.29 (s, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 141.8, 138.8, 138.2, 133.6, 129.4, 128.4, 128.4, 126.1, 124.4, 121.1, 43.7, 21.4.

MS (EI): m/z = 277 (100, M^+), 140 (32), 125 (43), 124 (94), 123 (81), 91 (47), 77 (66).

HRMS: m/z calcd for $[\text{C}_{14}\text{H}_{15}\text{NOS}_2 + \text{H}]^+$: 278.0668; found: 278.0668.

***N*-(Naphthalen-2-ylthio)-*S*-methyl-*S*-phenylsulfoximine (5aj)**

Yellow oil; yield: 48 mg (77%).

IR (ATR): 3461, 3308, 3052, 2924, 2665, 2327, 2092, 1914, 1738, 1584, 1445, 1399, 1211, 1140, 1090, 982, 813, 738, 684 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 7.98–7.95 (m, 2 H), 7.82–7.80 (m, 1 H), 7.75–7.67 (m, 3 H), 7.66–7.58 (m, 1 H), 7.57–7.54 (m, 2 H), 7.45–7.36 (m, 3 H), 3.31 (s, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 139.7, 138.7, 133.7, 131.6, 129.5, 128.4, 128.0, 127.7, 127.1, 126.3, 125.0, 122.7, 121.4, 43.8.

MS (EI): m/z = 313 (100, M^+), 159 (42), 140 (30), 127 (42), 125 (32), 124 (40), 77 (30).

HRMS: m/z calcd for $[\text{C}_{17}\text{H}_{15}\text{NOS}_2 + \text{H}]^+$: 314.0668; found: 314.0668.

***N*-(*tert*-Butylthio)-*S*-methyl-*S*-phenylsulfoximine (5ak)**

Colorless oil; yield: 10 mg (21%).

IR (ATR): 3272, 2962, 2291, 2094, 1933, 1592, 1408, 1257, 1017, 866, 769, 686 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 7.96–7.94 (m, 2 H), 7.64–7.60 (m, 1 H), 7.59–7.56 (m, 2 H), 3.14 (s, 3 H), 1.38 (s, 9 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ = 133.1, 129.5, 128.5, 45.5, 44.2, 31.3.

MS (EI): m/z = 243 (4, M^+), 186 (3), 140 (22), 125 (100), 89 (65), 77 (48).

HRMS: m/z calcd for $[\text{C}_{11}\text{H}_{17}\text{NOS}_2 + \text{H}]^+$: 244.0824; found: 244.0825.

***N*-(Cyclohexylthio)-*S*-methyl-*S*-phenylsulfoximine (5al)**

Pale yellow oil; yield: 16 mg (30%).

IR (ATR): 3319, 3223, 2923, 2119, 1837, 1454, 1314, 1142, 1076, 988, 724 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 7.92–7.90 (m, 2H), 7.65–7.62 (m, 1H), 7.59–7.56 (m, 2H), 3.18 (s, 3H), 3.00–2.97 (m, 1H), 2.12–2.10 (m, 1H), 1.99–1.98 (m, 1H), 1.80–1.73 (m, 2H), 1.62–1.59 (m, 2H), 1.33–1.22 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ = 139.4, 133.3, 129.4, 128.5, 50.3, 43.9, 31.4, 26.0, 25.9.

MS (EI): m/z = 269 (5, M^+), 186 (2), 140 (29), 139 (18), 125 (66), 124 (58), 77 (100).

HRMS (EI): m/z calcd for $[\text{C}_{16}\text{H}_{15}\text{NOS}_2]^+$: 269.0903; found: 269.0891.

***N*-(Phenylthio)-*S,S*-diphenylsulfoximine (5ba)¹⁵**

Colorless oil; yield: 50 mg (77%).

^1H NMR (600 MHz, CDCl_3): δ = 8.03–8.01 (m, 4 H), 7.59–7.53 (m, 2 H), 7.52–7.48 (m, 4 H), 7.44–7.42 (m, 2 H), 7.27–7.24 (m, 2 H), 7.09–7.07 (m, 1 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ = 142.1, 139.9, 133.2, 129.3, 128.5, 128.4, 125.0, 123.9.

***N*-(Phenylthio)-*S*-(4-fluorophenyl)-*S*-methylsulfoximine (5ca)**

Colorless oil; yield: 26 mg (46%).

IR (ATR): 3459, 3300, 3020, 2926, 2324, 2098, 1899, 1738, 1585, 1482, 1310, 1212, 1089, 980, 823, 736, 683 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 7.97–7.94 (m, 2 H), 7.39–7.37 (m, 2 H), 7.28–7.23 (m, 4 H), 7.11–7.09 (m, 2 H), 3.28 (s, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ = 165.9 (d, $J_{\text{C-F}}$ = 258.2 Hz), 141.8, 134.5, 131.3 (d, $J_{\text{C-F}}$ = 9.1 Hz), 128.5, 125.3, 124.0, 116.8 (d, $J_{\text{C-F}}$ = 22.7 Hz), 44.0.

MS (EI): m/z = 281 (34, M^+), 143 (6), 142 (4), 127 (40), 124 (100), 109 (5), 95 (17), 77 (30).

HRMS: m/z calcd for $[\text{C}_{13}\text{H}_{13}\text{FNOS}_2 + \text{H}]^+$: 282.0417; found: 282.0417.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0037-1610369>.

References

- (1) For selected reviews, see: (a) Johnson, C. R. *Aldrichimica Acta* **1985**, *18*, 3. (b) Reggelin, M.; Zur, C. *Synthesis* **2000**, 1. (c) Gais, H.-J. *Heteroat. Chem.* **2007**, *18*, 472. (d) Harmata, M. *Chemtracts* **2003**, *16*, 660. (e) Okamura, H.; Bolm, C. *Chem. Lett.* **2004**, *33*, 482. (f) Bull, J. A.; Degennaro, L.; Luisi, R. *Synlett* **2017**, *28*, 2525. (g) Hosseinian, A.; Fekri, L. Z.; Monfared, A.; Vessally, E.; Nikpassand, M. *J. Sulfur Chem.* **2018**, in press; DOI: 10.1080/17415993.2018.1471142.
- (2) For representative contributions, see: (a) Sparks, T. C.; Loso, M. R.; Babcock, J. M.; Kramer, V. J.; Zhu, Y.; Nugent, B. M.; Thomas, J. D. *Modern Crop Protection Compounds*; Kraemer, W.; Schirmer, U.; Jeschke, P.; Witschel, M., Eds.; Wiley-VCH: Weinheim, **2012**, 1226. (b) Arndt, K. E.; Bland, D. C.; Irvine, N. M.; Powers, S. L.; Martin, T. P.; McConnell, J. R.; Podhorez, D. E.; Renga, J. M.; Ross, R.; Roth, G. A.; Scherzer, B. D.; Toyzan, T. W. *Org. Process Res. Dev.* **2015**, *19*, 454. (c) Lücking, U. *Angew. Chem. Int. Ed.* **2013**, *52*, 9399. (d) Frings, M.; Bolm, C.; Blum, A.; Gnam, C. *Eur. J. Med. Chem.* **2017**, *126*, 225.
- (3) Trost, B. M.; Matsuoka, R. T. *Synlett* **1992**, 27.
- (4) Bizet, V.; Hendriks, C. M. M.; Bolm, C. *Chem. Soc. Rev.* **2015**, *44*, 3378.
- (5) (a) Bizet, V.; Kowalczyk, R.; Bolm, C. *Chem. Soc. Rev.* **2014**, *43*, 2426. (b) Shen, X.; Hu, J. *Eur. J. Org. Chem.* **2014**, 4437.
- (6) Oae, S.; Harada, K.; Tsujihara, K.; Furukawa, N. *Int. J. Sulfur Chem., Part A* **1972**, *2*, 49.
- (7) Goldberg, F. W.; Kettle, J. G.; Xiong, J.; Lin, D. *Tetrahedron* **2014**, *70*, 6613.
- (8) For a sulfoxide to sulfilimine conversion followed by oxidation to give sulfoxides, see: Hendriks, C. M. M.; Lamers, P.; Engel, J.; Bolm, C. *Adv. Synth. Catal.* **2013**, *355*, 3363.
- (9) For direct approaches towards NH-sulfoximines, see: (a) Zenzola, M.; Doran, R.; Degennaro, L.; Luisi, R.; Bull, J. A. *Angew. Chem. Int. Ed.* **2016**, *55*, 7203. (b) Tota, A.; Zenzola, M.; Chawner, S. J.; St. Jon-Campbell, S.; Carlucci, C.; Romanazzi, G.; Degennaro, L.; Bull, J. A.; Luisi, R. *Chem. Commun.* **2017**, *53*, 348. (c) Yu, H.; Zhen, L.; Bolm, C. *Angew. Chem. Int. Ed.* **2018**, *57*, 324.
- (10) For selected examples from our group, see: N-arylation: (a) Bolm, C.; Hildebrand, J. P. *J. Org. Chem.* **2000**, *65*, 169. (b) Miyasaka, M.; Hirano, K.; Satoh, T.; Kowalczyk, R.; Bolm, C.; Miura, M. *Org. Lett.* **2011**, *13*, 359. N-Alkynylation: (c) Wang, L.; Huang, H.; Priebbenow, D. L.; Pan, F.; Bolm, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 3478. (d) Priebbenow, D. L.; Becker, P.; Bolm, C. *Org. Lett.* **2013**, *15*, 6155. N-Acylation: (e) Cheng, H.; Bolm, C. *Synlett* **2016**, 27, 769. N-Alkylation: (f) Hendriks, C. M. M.; Bohmann, R. A.; Bohlem, M.; Bolm, C. *Adv. Synth. Catal.* **2014**, *356*, 1847. (g) Wang, H.; Zhang, D.; Bolm, C. *Angew. Chem. Int. Ed.* **2018**, *57*, 5863.
- (11) Wang, H.; Cheng, Y.; Becker, P.; Raabe, G.; Bolm, C. *Angew. Chem. Int. Ed.* **2016**, *55*, 12655.
- (12) For related hypervalent iodine reagents having a 1,2-benziodoxole core, see: Wang, H.; Zhang, D.; Sheng, H.; Bolm, C. *J. Org. Chem.* **2017**, *82*, 11854.
- (13) For an alternative reaction behavior of such species, see: Wang, H.; Zhang, D.; Bolm, C. *Chem. Eur. J.* **2018**, in press; DOI: org/10.1002/chem.201803975.
- (14) (a) Buchholt, H. C. *Org. Prep. Proced. Int.* **1970**, *2*, 177. (b) Akutagawa, K.; Furukawa, N.; Oae, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 518.
- (15) Zhu, H.; Yu, J. T.; Cheng, J. *Chem. Commun.* **2016**, *52*, 11908.
- (16) (a) Peng, Y.; Lin, Y.; Nie, R.; Zheng, Y.; Liu, Y.; Guo, L.; Wu, Y. *Eur. J. Org. Chem.* **2018**, 844. (b) Yang, L.; Feng, J.; Qiao, M.; Zeng, Q. *Org. Chem. Front.* **2018**, *5*, 24.
- (17) For the preparation of sulfoximines with N-SCF₃ groups, which were prepared by reacting NBr-sulfoximines with AgSCF₃, see: Bohnen, C.; Bolm, C. *Org. Lett.* **2015**, *17*, 3011.
- (18) In these experiments, combinations of **4a** (2 equiv) and NaH (2.1 equiv) were applied; satisfying results were not achieved in DCE at r.t. or 50 °C or in CH₂Cl₂ at 50 °C.
- (19) For selected overviews on hypervalent iodine reagents, see: (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523. (b) Singh, F. V.; Wirth, T. *Chem. Asian J.* **2014**, *9*, 950. (c) Ochiai, M. *Chem. Rec.* **2007**, *7*, 12. (d) Uyanik, M.; Ishihara, K. *ChemCatChem* **2012**, *4*, 177. (e) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299. (f) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328. (g) Zhdankin, V. V. *Hypervalent Iodine Chemistry: Preparation, Structure and Synthetic Application of Polyvalent Iodine Compounds*; Wiley: New York, **2013**. (h) *Hypervalent Iodine Chemistry*, In *Topics in Current Chemistry*; Wirth, T., Ed.; Springer: Switzerland, **2015**.
- (20) (a) Tinnis, F.; Stridfeldt, E.; Lundberg, H.; Adolfsson, H.; Olofsson, B. *Org. Lett.* **2015**, *17*, 2688. (b) Malmgren, J.; Santoro, S.; Jalalian, N.; Himo, F.; Olofsson, B. *Chem. Eur. J.* **2013**, *19*, 10334.