153. Structure and Reactivity of a Sulfoximine-Stabilized Chiral Dilithiocarbanion

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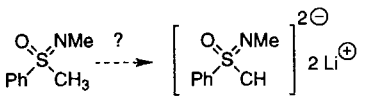
The synthesis and X-ray analysis of a racemic dilithiated *S*-ethyl-*N*-methyl-*S*-phenylsulfoximine cluster **2** with *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA) as coordinating solvent is presented. The lithium complex **2** consists of a mixed tetrameric mono- and dilithio salt. Unexpectedly, a separation of the enantiomers in mono- and dilithiated antipodes with respect to the chirality center on the S-atom is observed. Dilithiation of *S*-ethyl-*N*-methyl-*S*-phenylsulfoximine (**1**) affords a chiral dinucleophile which undergoes highly regio- and stereoselective alkylation reactions with bis-electrophiles.

Introduction. – Multiple C–C bond formation in one reaction step represents a challenge in organic synthesis which may be achieved successfully by the use of dimetallated intermediates and their subsequent treatment with bis-electrophiles [1]. The structural investigation of such dimetallated compounds by X-ray analysis and theoretical calculations has led to a great body of information in the case of dilithiated hydrocarbons [2], but they are still in their infancy in the case of heteroatom-stabilized dilithiocarbanions [3]. In particular, little structural information is available for chiral dilithio compounds [4], in contrast to chiral heteroatom-stabilized monolithiocarbanions which are better investigated [2] [3] [5]. In certain cases, a structure-reactivity-selectivity relationship has been established, which facilitates a rationalization of the stereochemical outcome in asymmetric transformations leading finally to an optimal design of the chiral reagent and an enhancement of stereocontrol [6]. Heteroatom-stabilized organic dilithio salts are known to act as dinucleophiles in multiple C–C bond formation reactions or as supernucleophiles in the reaction with poor electrophiles [1]. The theoretical expectation that a chiral modification of such dimetallated compounds would lead to reagents which are able to undergo multiple C–C bond formations in a stereoselective manner has not yet been proven [4]. To do so, we chose the sulfoximine group, the chiral aza analogue of the sulfones, as a configurationally stable chiral functional group, intending to create such a dilithio species (see *Scheme 1*).

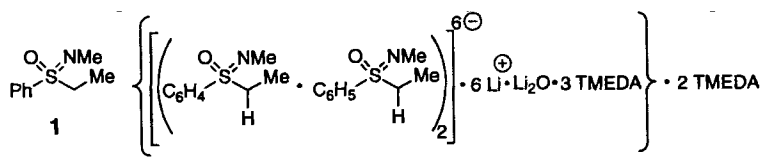
Scheme 1



Simple monolithio salts of these chiral sulfur compounds have demonstrated a widespread synthetic use in asymmetric synthesis, but hitherto nothing is known about the structures and the reactions with dilithiated sulfoximines [7] (a *N*,*C*-dilithiated sulfox-

imine has previously been used in cyclization reactions [8]). This is in contrast to the dilithio salts of various sulfones which are already valuable intermediates in organic synthesis and show a broad range of applications [9]. Another important aspect stems from the potential attenuation of chirality in the reaction of such chiral substituted dianions with prochiral bis-electrophiles. In the following, we report our results concerning the structure determination of a dilithiated sulfoximine in the solid state and its reactions with bis-electrophiles.

Results and Discussion. – Treatment of *racemic* *S*-ethyl-*N*-methyl-*S*-phenylsulfoximine (**1**) with 2 equiv. of BuLi in *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA) in the presence of Li_2O at −78° to 25° yields a species **2**, a mixed aggregate containing mono- and dilithiated *S*-ethyl-*N*-methyl-*S*-phenylsulfoximine units in a 2:2 ratio coordinated by 3 TMEDA ligands. The aggregate **2** crystallizes in the space group *C*2/*c*, and the unit cell contains four clusters together with eight disordered TMEDA molecules. The unit cell contains two clusters, each composed of two sulfoximine dianions in the (*R*) configuration and two sulfoximine monoanions in the (*S*) configuration (*Figs. 1* and *2*; see *Tables 1* and *2* for selected bond lengths and angles). Since the lattice is centrosymmetric, there are two clusters in which these configurations are reversed. That means an internal chiral resolution has taken place within the clusters.



2 TMEDA = $Me_2NCH_2CH_2NMe_2$

The dianionic subunit is characterized by two Li–C contacts of the *ortho*-C(36) atom forming five-membered ring chelates (involving Li(2) and Li(4)) with the heteroatoms at the S-atom, as indicated in **A** (see also *Table 1*). For Li(2), a coordination to the sulfoximine O(21) atom, a single O(22) atom derived from Li_2O, and a C(α) (= C(1)) atom of the neighboring sulfoximine monoanion is found, whereas Li(4) is coordinated to the sulfoximine N(21) atom, the O-atom of the Li_2O core, and a N(22) atom of one TMEDA ligand. For such an *ortho*-directing effect in sulfoximines, only little data exist in contrast to the situation in sulfones which are known to be powerful *ortho*-directing moieties [10]. In spite of being deprotonated, a Li–C bond to the C(α) (= C(21)) atom is not observed. This is consistent with a substantial S–C multiple-bond character, which lowers the basic character of this C(α) atom. This view is supported by a short S–C(α) (= S(21)–C(21)) distance of 1.62 Å (*vs.* 1.73 Å in non-deprotonated sulfoximines [11]). The anionic C(α) atom has a nearly planar configuration as illustrated by the angle S(21)–C(21)–C(22) (122.0°). In contrast to monolithiated sulfoximines, the lone pair at C(α) adopts a conformation in which it is oriented between the imino N-atom and the phenyl group instead of being *gauche* to both heteroatoms [11].

The center of the aggregate is characterized by a distorted octahedral Li_6O unit **C** due to incorporated Li_2O. In certain cases, Li_2O has been observed in crystalline organolithium compounds [12]. It has been pointed out that contamination of the commercially

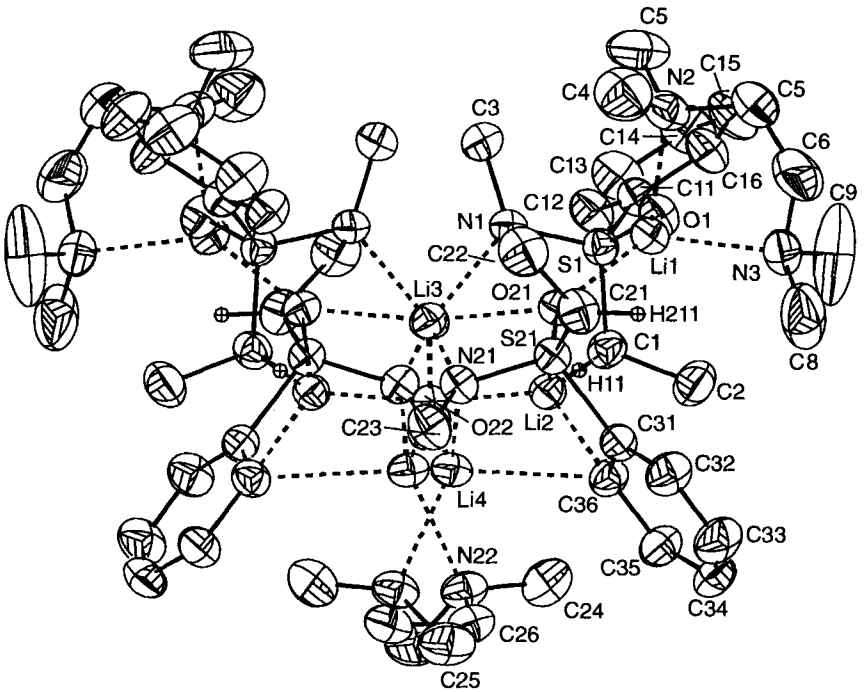


Fig. 1. *Molecular structure of tetrameric* **2**. Two disordered TMEDA molecules and the H-atoms are omitted for clarity, except H(11) and H(211) which are in localized positions; arbitrary numbering.

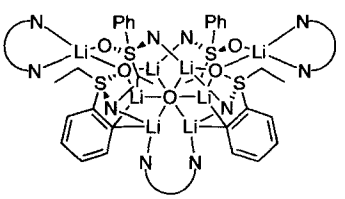


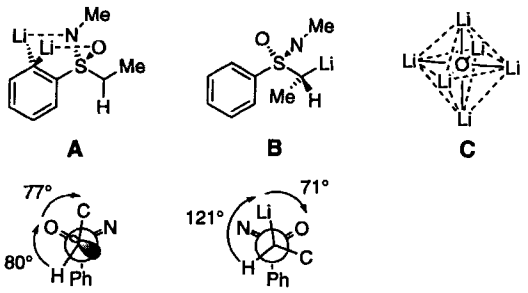
Fig. 2. *Schematic presentation of tetrameric* **2**. The Me groups bound to the N-atoms of the TMEDA ligands and to the sulfoximine N-atoms have been omitted for clarity.

Table 1. *Selected Bond Length* [Å] *of* **2**. Arbitrary numbering, see *Fig. 1.*

Li(1)–O(1)	1.952(6)	Li(2)–C(36)	2.240(6)	Li(3)–O(21)	2.135(5)	S(21)–O(21)	1.533(2)
Li(1)–N(1)	2.214(6)	Li(4)–C(36)	2.540(6)	Li(4)–N(22)	2.162(6)	S(21)–N(21)	1.572(3)
Li(2)–O(21)	2.166(6)	S(1)–O(1)	1.474(2)	Li(4)–N(21)	2.188(6)	S(21)–C(21)	1.616(3)
Li(2)–O(22)	1.918(5)	S(1)–N(1)	1.528(3)	Li(2)–C(1)	2.249(6)		
Li(3)–N(1)	1.978(5)	S(1)–C(1)	1.664(3)				

Table 2. *Selected Angles* [°] *and Dihedral Angles* [°] *of* **2**. Arbitrary numbering, see *Fig. 1.*

S(1)–C(1)–H(11)	111.0(24)	O(21)–S(21)–C(21)	120.0(2)	H(11)–C(1)–S(1)–N(1)	63.3(23)
C(2)–C(1)–H(11)	105.1(25)	O(21)–S(21)–N(21)	100.3(1)	H(11)–C(1)–S(1)–O(1)	167.6(22)
S(21)–C(21)–H(211)	103.4(25)	C(2)–C(1)–Li(2)	109.4(3)	N(21)–S(21)–C(21)–H(211)	162.1(31)
C(22)–C(21)–H(211)	129.3(25)	H(11)–C(1)–Li(2)	112.9(25)	N(21)–S(21)–C(21)–C(22)	41.4(4)
O(1)–S(1)–C(1)	109.8(2)	C(2)–C(1)–S(1)–N(1)	177.4(3)	O(21)–S(21)–C(21)–C(22)	76.7(5)
O(1)–S(1)–N(1)	118.4(2)	C(2)–C(1)–S(1)–O(1)	48.3(3)	O(21)–S(21)–C(21)–H(211)	79.8(33)

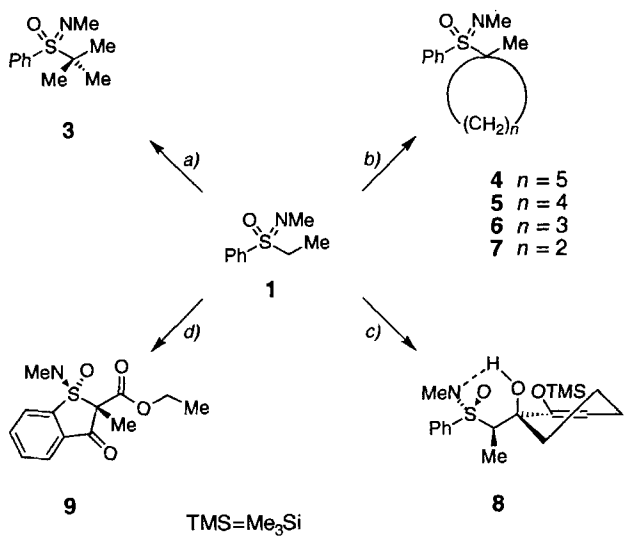


supplied alkyllithium reagent with LiOH leads to the formation and inclusion of Li_2O upon treatment of an organic substrate [12].

In the monoanionic sulfoximine moiety, a Li(2)–C(α) (Li(2)–C(1)) contact is observed (2.25 Å), whereas the two heteroatoms are coordinating to two other Li^+ cations, an arrangement unknown for monolithiated sulfoximines (see **B**) [11]. In this case, the C(α) atom has a distinct pyramidal configuration as supported by the angles around C(1) (see *Table 2*). A *Newman* projection along the S–C(α) (= S(1)–C(1)) bond of **B** shows that the C(α)–Li bond is arranged in a *gauche* conformation between the N- and O-atoms of the sulfoximine moiety. The coordination sites of the Li(1) atom bonded to the sulfoximine O(1) of **B** are occupied by two N-atoms of the TMEDA ligands and the O(21) atom of the dilithiated sulfoximine moiety **A** which leads to a bridging of the mono- and dilithio sulfoximine units. The Li(3) atom connected to the sulfoximine N(1) of **B** shows links to the N(21) and O(21) atoms of the dilithiated sulfoximine **A** and to the O-atom of the Li_6O octahedron **C**. A significant shortening of the S–C(α) bond is found in the monoanion **B** S(1)–C(1) (1.66 Å *vs.* 1.73 Å in non-deprotonated sulfoximines [11]), but not as pronounced as for the dianionic species **A** where the S–C(α) bond length is 1.62 Å. This additional contraction in the dianion **A** can be explained with the threefold and twofold Li coordination of the sulfoximine O(21) and N(21) atoms, respectively, which leads to an increased coulombic attraction of the negatively charged C(α) (= C(21)) atom [3].

For the investigation of the use of a chiral dilithiated sulfoximine in asymmetric synthesis, the generated dilithio intermediate was trapped with various bis-electrophiles. Addition of MeI afforded nearly regioselectively the α,α-dimethylated sulfoximine **3** in high yield; *Scheme 2* (85%). Only traces of an α,*ortho*-dialkylated product could be detected by GC/MS (< 3%). Such a behavior is unknown for sulfoximines, but is not unusual for sulfones; indeed an α,*ortho*-dilithiated sulfone-derived species has been observed which showed a similar reactivity towards alkylation with alkyl halides [13]. NMR-Spectroscopic studies by *Gais* and coworkers have shown that a temperature-dependent transmetallation of an α,*ortho* to α,α-dilithio species is possible [13] [14]. Thus, it becomes reasonable to suggest a transmetallation process as a possible explanation for the observed regioselectivity with dilithiated **1**. That means, after the first alkylation step in the α-position, a translithiation takes place leading finally to the α,α-dialkylated product. Performing this procedure with a bis-electrophile like 1,5-diiodopentane, we expected a similar regioselectivity to the reaction with MeI, which should lead to a ring closure in the α-position. Indeed a six-membered ring **4** is formed without any regioisomers but in high yield (81%; *Scheme 2*). With 1,4-diiodobutane, a five-membered ring

Scheme 2



a) BuLi (2 equiv.), MeI (2 equiv.), THF, 0°; 85%. *b*) BuLi (2 equiv.), 1,5-diiodopentane (n = 5), 1,4-diiodobutane (n = 4), 1,3-dichloropropane (n = 3), or 1,2-dichloroethane (n = 2), THF, 0°; **4**, 81%; **5**, 76%; **6**, 27%; **7**, 11%. *c*) BuLi (2 equiv.), cyclohexane-1,2-dione, Me_3SiCl (2 equiv.), THF, 0°; 72%. *d*) BuLi (2 equiv.), ethyl carbonochloridate (2 equiv.), THF, 0°; 63%.

species **5** was obtained in good yield (76%). Cyclization reactions with shorter-chain bis-electrophiles showed dramatically lower yields, due to the increased strain in these small ring systems. Thus, the cyclobutyl derivative **6** and the cyclopropyl-sulfoximine **7** were only accessible in yields of 27 and 11%, respectively.

In contrast to the simple bis-electrophiles mentioned above, cyclohexane-1,2-dione did not undergo, in the presence of Me_3SiCl, ring closure to a cyclopropane derivative. Instead the α,*ortho*-dilithio species **2** acted as a base and nucleophile leading in a *synergistic* manner in a single step to the β-hydroxysulfoximine-derived silyl enol ether **8** in high yield (72%) and high diastereoisomeric ratio (95:5). The absolute configuration of the major isomer of **8** was determined by X-ray structure analysis (*Fig. 3*). Typical of β-hydroxysulfoximines is the ability to build intramolecular H-bonds to the imino N-atom giving a six-membered ring with a chair conformation [15]. The Me group at C(α) and the larger, silyloxy-containing substituent at C(β) are oriented in a pseudoequatorial fashion.

The reaction of the dilithiosulfoximine **2** with ethyl carbonochloridate afforded in good yield (63%) the heterocycle **9** as single diastereoisomer. This cyclization must proceed *via* a third deprotonation step. NOE Experiments confirmed the *cis*-configuration of the two Me groups at the five-membered heterocycle of **9**. We are now pursuing novel applications of these dilithio compounds in asymmetric synthesis.

Conclusion. – In summary, we have introduced a new methodology for the single-step formation of multiple C–C bonds which proceeds with high regio- and diastereoselectivity. The reaction of the dilithiated sulfoximine **1** with cyclohexane-1,2-dione afforded the

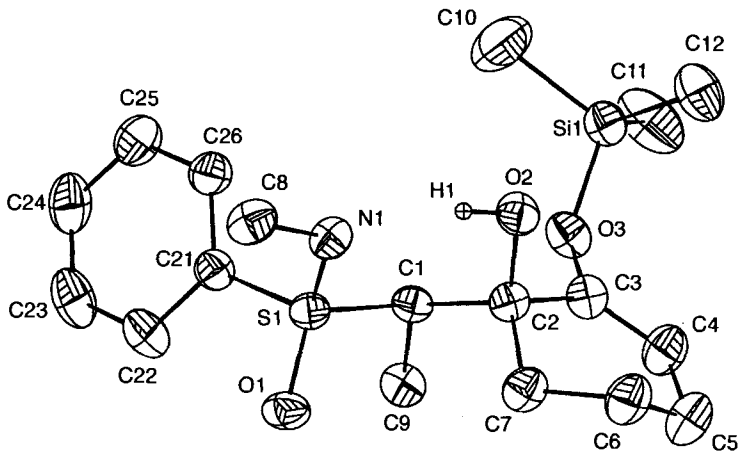


Fig. 3. *Molecular structure of* **8**. H-Atoms are omitted for clarity, except for H(1).

Table 3. *Selected Intramolecular Distances* [Å] *and Angles* [°] *of* **8**

	Distances		Angles		Distances		Angles
S(1)–O(1)	1.450(2)	N(1)–S(1)–O(1)	121.5(1)	C(2)–C(3)	1.522(3)	C(1)–S(1)–C(21)	102.2(1)
S(1)–N(1)	1.521(2)	N(1)–S(1)–C(1)	104.4(1)	C(3)–C(4)	1.315(4)	C(2)–C(3)–C(4)	124.0(2)
S(1)–C(1)	1.806(2)	O(1)–S(1)–C(1)	111.2(1)	C(2)–O(2)	1.431(3)	C(2)–C(3)–O(3)	114.4(2)
S(1)–C(21)	1.789(3)	N(1)–S(1)–C(21)	110.7(3)	C(3)–O(3)	1.382(3)	C(4)–C(3)–O(3)	121.6(2)
C(1)–C(2)	1.551(3)	O(1)–S(1)–C(21)	105.3(1)	O(3)–Si(1)	1.644(2)	C(3)–C(4)–C(5)	123.9(3)

β-hydroxysulfoximine-derived silyl enol ether **8** with high diastereoselectivity, whereas a highly reactive electrophile such as ethyl carbonochloridate allowed access to a new heterocyclic system **9**. The crystal structure of the mixed tetrameric lithium cluster **2**, which is related to the dilithio intermediate in the afore-mentioned reactions, was determined. We observed a seperation of the enantiomers in mono- and dilithiated antipodes with respect to the chirality center at the S-atom. The dilithio unit in **2** can be regarded as an α,*ortho*-dilithiosulfoximine. Such an *ortho*-directing effect has been unknown for sulfoximines. Finally, C(α) of the dilithio unit in **2** shows no contact to a Li^+ cation which is due to its decreased basicity and the significant shortening of the S–C(α) bond.

Experimental Part

General. All reactions were carried out under Ar in flame-dried glassware using syringe techniques. *N,N,N',N'*-Tetramethylethane-1,2-diamine (TMEDA) was distilled from CaH_2 and tetrahydrofurane (THF) from Na/benzophenone ketyl. BuLi was purchased from *Fluka* and titrated according to [16]. ^{1}H-NMR Spectra *Varian Gemini* (300 MHz) spectrometer at r.t.; δ in ppm rel. to internal $SiMe_4$ (= 0 ppm), *J* in Hz. ^{13}C-NMR Spectra: *Varian Gemini* (75 MHz) spectrometer; solvent as internal standard ($CDCl_3$ at 77.0 ppm).

2. {*Hexalithium Bis{1-[S-(benzen-2-id-1-yl)-*N*-methylsulfonimidoyl]ethan-1-ide} Bis[1-(*N*-methyl-*S*-phenylsulfonimidoyl)ethan-1-id]*} – *(Lithium Oxide)* – (N,N,N',N'-*Tetramethylethane-1,2-diamine) (1/1/5)* (**2**). To a soln. of **1** (200 mg, 1.09 mmol) in TMEDA (2.5 ml), 1.55M BuLi in hexane (1.5 ml, 2.3 mmol) was slowly added at –78°. The mixture was allowed to warm up to 25°, and after 48 h, yellow single crystals of **2** were grown (74 mg, 20%) which were suitable for X-ray analysis.

3. *X-Ray Analysis of* **2** *and* **8**. The aggregate **2** crystallizes in the monoclinic space group $C2/c$ as cube-shaped, yellow crystals and **8** in the monoclinic space group $P2_1$. Of **2**, a sample with the dimensions of $0.3 \times 0.5 \times 0.7$ mm was sealed in a glass capillary and mounted on the diffractometer. A single crystal of **8** was measured under the same conditions. Unit-cell parameters were determined by carefully centering 25 independent, strong reflections with $19° \leq \Theta \leq 42°$. Data collection was carried out at 293 K using an *Enraf-Nonius-CAD4* diffractometer equipped with a CuK_α fine focus sealed tube ($\lambda = 1.54180$ Å) and with a graphite monochromator. For compound **2** three reflections were monitored every 2 h, which showed an intensity loss of 25%. This decay, even though high, was linear and is attributed to the high reactivity of the compound. For **2**, a spherical absorption correction was applied. For **8**, φ-scans were used to determine the absorption. The structures were solved by direct methods using the program SIR92 [17]. Anisotropic least squares full matrix refinement was carried out on all non H-atoms using the program CRYSTALS [18]. The disordered TMEDA ligands were refined using restraints. The H-atoms bonded to the C(α) atoms in **2** were localized in the difference map and refined restraining the C–H distance to 0.96 Å; the same procedure was applied for H(1) in compound **8**. All other H-atoms were in calculated positions. *Chebychev* polynomial weights were used to complete the refinement [19]. Scattering factors were taken from the 'International Tables for X-Ray Crystallography' (Vol. IV, Table 2.2B). E.s.d.s for the given dihedral angles of **2** were calculated using the XTAL program [20]. Crystal data and other numerical details of the structure determinations are listed in *Table 4*.

Table 4. *Experimental Data for the X-Ray Diffraction Studies of* **2** *and* **8**

	2	**8**
Formula	$C_{66}H_{126}Li_8N_{14}O_5S_4$	$C_{18}H_{29}NO_3SSi$
Space group	$C2/c$	$P2_1$
a [Å]	25.9516(17)	6.5089(4)
b [Å]	12.1283(12)	14.9724(10)
c [Å]	26.8329(6)	11.0878(5)
α [°]	90	90
β [°]	90.218(3)	105.395(4)
γ [°]	90	90
Volume [Å^3]	8445(1)	1041.78(1)
Z	4	2
Crystal dimensions [mm]	$0.3 \times 0.5 \times 0.7$	$0.1 \times 0.4 \times 0.5$
Temperature [K]	293	293
Θ_{max}	64.97	74.33
Radiation	CuK_α ($\lambda = 1.54178$ Å)	CuK_α ($\lambda = 1.54178$ Å)
Scan mode	$\omega/2\Theta$	$\omega/2\Theta$
μ [cm^{-1}]	1.38	2.03
Max./min. transmission	1/0.98	1/0.61
No. of independent refl.	6169	2165
No. of refl. incl. in refinement	4826, ($F > 3\sigma(F)$)	2108 ($F > 3\sigma(F)$)
No. of parameters	521	223
R ($\cdot$ 100%)	6.88	2.98
R_w ($\cdot$ 100%)	8.57	3.72
$\Delta\rho$ [e Å^{-3}]	0.43/ – 0.34	0.20/ – 0.14
Weighting scheme	$\omega \cdot (1 - (\delta F/6\sigma F)^2)^2$	
R/Value	$R = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$	
R_w/Value	$R_w = \{\sum(\|F_o\| - \|F_c\|)^2 \cdot \omega)/\sum F_o^2 \cdot \omega\}^{1/2}$	

4. *General Procedure* (GP) *for Trapping Reactions with Bis-electrophiles*. To a soln. of **1** (1 g, 5.46 mmol) in dry THF (40 ml), 1.37M BuLi in hexane (7.97 ml, 10.9 mmol) was added at –78°. The mixture was allowed to warm up to 0° (→ deep orange). Then a soln. of a electrophile (2 equiv.) or bis-electrophile (1 equiv.) in THF (1 ml) was added dropwise. After stirring for 2 h at 0°, the mixture was treated with sat. $NaHCO_3$ soln. and extracted with AcOEt. The org. layer was dried (Na_2SO_4) and evaporated. The residue was purified by FC to afford the alkylated sulfoximines.

(±)-S-*(*tert-*butyl)*-N-*methyl*-S-*phenylsulfoximine* (**3**). With MeI (0.68 ml, 10.9 mmol) as electrophile according to the *GP*. FC (AcOEt/hexane 1:1, R_f 0.23) afforded **3** (0.97 g, 85%). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.38 (*s*, *t*-Bu); 2.69 (*s*, MeN); 7.52–7.64 (*m*, 3 arom. H); 7.78–7.83 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.99, 29.78, 59.87, 128.84, 131.72, 132.59, 133.3. EI-MS (70 eV): 211 (3), 155 (70), 138 (18), 125 (63), 107 (97), 97 (27), 78 (100), 57 (55), 41 (28). Anal. calc. for $C_{11}H_{17}NOS$ (211.32): C 62.52, H 8.11, N 6.63; found: C 62.41, H 8.28, N 6.34.

(±)-N-*Methyl*-S-*(1-methylcyclohexyl)*-S-*phenylsulfoximine* (**4**). With 1,5-diiodopentane (0.74 ml, 5.46 mmol) as bis-electrophile according to the *GP*. FC (AcOEt/hexane 1:1, R_f 0.41) afforded **4** (1.1 g, 81%). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.1–1.4 (*m*, 4 H); 1.35 (*s*, Me); 1.55–1.97 (*m*, 6 H); 2.69 (*s*, MeN); 7.51–7.62 (*m*, 3 arom. H); 7.75–7.80 (*dm*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.01, 21.67, 21.71, 24.99, 29.66, 29.76, 29.95, 63.60, 128.71, 131.85, 132.42, 133.79. EI-MS (70 eV): 251 (4), 221 (6), 155 (90), 125 (58), 107 (93), 78 (93), 55 (100). Anal. calc. for $C_{14}H_{21}NOS$ (251.39): C 66.89, H 8.42, N 5.57; found: C 66.41, H 8.37, N 5.27.

(±)-N-*Methyl*-S-*(1-methylcylcopentyl)*-S-*phenylsulfoximine* (**5**). With 1,4-diiodobutane (0.65 ml, 5.46 mmol) as bis-electrophile according to the *GP*. FC (AcOEt/hexane 1:1, R_f 0.3) afforded **5** (0.99 g, 76%). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.39 (*s*, Me); 1.55–1.81 (*m*, 6 H); 2.35–2.48 (*m*, 1 H); 2.50–2.63 (*m*, 1 H); 2.71 (*s*, MeN); 7.50–7.67 (*m*, 3 arom. H); 7.81–7.87 (*dm*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.77, 25.01, 25.19, 29.68, 34.71, 34.80, 69.27, 128.85, 121.27, 132.45, 135.29. EI-MS (70 eV): 237 (4), 155 (84), 138 (23), 83 (31), 69 (28), 55 (46). Anal. calc. for $C_{13}H_{19}NOS$ (237.36): C 65.78, H 8.07, N 5.90; found: C 65.50, H 8.17, N 5.90.

(±)-N-*Methyl*-S-*(1-methylcyclobutyl)*-S-*phenylsulfoximine* (**6**). With 1,3-dichloropropane (0.52 ml, 5.46 mmol) as bis-electrophile according to the *GP*. FC (AcOEt/hexane 1:1, R_f 0.29) afforded **6** (0.33 g, 27%). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.46 (*s*, Me); 1.50–1.61 (*m*, 1 H); 1.78–2.0 (*m*, 3 H); 2.65 (*s*, MeN); 2.78–2.98 (*m*, 2 H); 7.45–7.60 (*m*, 3 arom. H); 7.71–7.77 (*dm*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.15, 21.43, 27.93, 28.38, 29.29, 61.27, 128.85, 130.66, 132.46, 134.23. EI-MS (70 eV): 223 (2), 155 (65), 138 (29), 125 (51), 107 (69), 78 (74), 69 (93), 51 (31). Anal. calc. for $C_{12}H_{17}NOS$ (223.34): C 64.54, H 7.67, N 6.27; found: C 64.14, H 7.74, N 6.09.

(±)-N-*Methyl*-S-*(1-methylcycloproypl)*-S-*phenylsulfoximine* (**7**). With 1,2-dichloroethane (0.43 ml, 5.46 mmol) as bis-electrophile according to the *GP*. FC (AcOEt/hexane 1:1, R_f 0.23) afforded **7** (0.12 g, 11%). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.56–0.64 (*m*, 1 H); 0.82–0.91 (*m*, 1 H); 1.38 (*s*, Me); 1.41–1.50 (*m*, 1 H); 1.67–1.76 (*m*, 1 H); 2.75 (*s*, MeN); 7.50–7.62 (*m*, 3 arom. H), 7.80–7.83 (*dm*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.86, 13.21, 18.84, 29.51, 36.56, 129.01, 129.83, 132.47, 138.50. EI-MS (70 eV): 209 (19), 154 (38), 125 (60), 106 (81), 77 (100), 55 (95). Anal. calc. for $C_{11}H_{15}NOS$ (209.31): C 63.12, H 7.22, N 6.69; found: C 63.01, H 7.33, N 6.51.

(±)-N-*Methyl*-S-*phenyl*-S-*{1-{1-hydroxy-2-[(trimethylsilyl)oxy]cyclohex-2-enyl}ethyl}sulfoximine* (= *1-[1-(*N-*Methyl*-S-*phenylsulfonimidoyl)ethyl]-2-[(trimethylsilyl)oxy]cyclohex-2-en-1-ol*; **8**). With cyclohexane-1,2-dione (0.61 g, 5.46 mmol) as bis-electrophile and Me_3SiCl (2 equiv.) according to the *GP*. FC (AcOEt/hexane 1:1, R_f 0.42) afforded **8** (1.44 g, 72%). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.18 (*s*, Me_3Si); 1.05 (*d*, J = 7, 3 H); 1.58–2.05 (*m*, 5 H); 2.40–2.50 (*m*, 1 H); 2.58 (*s*, MeN); 3.67 (*q*, $J \approx 7$, 1 H); 4.80 (*m*, 1 H); 7.46 (*s*, 1 H); 7.52–7.67 (*m*, 3 arom. H); 7.82–7.9 (*dm*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 0.39, 10.87, 17.23, 24.09, 29.23, 31.88, 63.23, 76.18, 108.68, 129.39, 129.57, 132.93, 137.46, 149.45. EI-MS (70 eV): 367 (0.3), 352 (2), 278 (1), 257 (1), 242 (2), 228 (25), 183 (7), 169 (20), 125 (11), 94 (23), 77 (13), 73 (100). Anal. calc. for $C_{18}H_{29}NO_3SSi$ (367.58): C 58.39, H 7.68, N 3.54; found: C 58.82, H 7.95, N 3.81.

(±)-Ethyl 2,3-Dihydro-2-methyl-3-oxobenzo[1]thiophene-2-acetic Acid 1-Methylimide 1-Oxide (**9**). With ethyl carbonochloridate (1.1 ml, 10.9 mmol) as electrophile according to the *GP*. FC (AcOEt/hexane 1:1, R_f 0.15) afforded **9** (0.96 g, 63%). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*t*, Me); 1.86 (*s*, Me); 3.38 (*s*, MeN); 4.02–4.18 (*m*, 2 H); 7.65 (*tm*, 1 arom. H); 7.67–7.78 (*m*, 2 arom. H); 7.83 (*dm*, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.27, 13.81, 33.85, 64.04, 72.82, 120.42, 122.24, 131.21, 134.50, 136.05, 136.53, 152.2, 177.05. EI-MS (70 eV): 281 (38), 218 (5), 179 (49), 147 (52), 136 (97), 108 (24), 91 (33), 56 (100), 43 (53). Anal. calc. for $C_{13}H_{15}NO_4S$ (281.33): C 55.50, H 5.37, N 4.98; found: C 54.95, H 5.69, N 4.77.

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