Addition Reactions of Sulfenyl and Sulfinyl Chlorides with 3-Phenyl-1-azabicyclo[1.1.0]butane

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The reactions of 3-phenyl-1-azabicyclo[1.1.0]butane with α-chlorosulfenyl chlorides and sulfinyl chlorides lead to the corresponding sulfenamides and sulfinamides, respectively, which possess an azetidine ring. It is proposed that a two-step mechanism occurs involving an intermediate carbenium ion, which is formed by the addition of the electrophile at the N-atom and cleavage of the N(1)–C(3) bond. The structures of **9b** and **10b** are established by X-ray crystallography.

1. Introduction. – Strained 1-azabicyclo[1.1.0]butanes **1** easily undergo cleavage of the N(1)–C(3) bond in the presence of reagents of type EX (E = electrophile, X = halogen, azide, acetate, *etc.*) to give azetidine derivatives **3** *via* a carbenium ion **2**, which combines with the nucleophile X [1–4] (*Scheme 1*). In the case of TsN_3 or TsCl, the cation **2** can be intercepted in a competitive reaction by a second molecule of **1** to form biazetidine derivatives **5** [5][6]. Similarly, the formation of 'dimeric' products was reported for the reaction of **1a** with butyl nitrite in AcOH [7] and of **1b** with N_2O_4 in the presence of atmospheric O_2 [8]. On the other hand, treatment of **1a** with triethyloxonium tetrafluoroborate led to the formation of polymeric products [9].

In the case of the unsubstituted 1-azabicyclo[1.1.0]butane (**1**, R = H), the addition of TsCl was reported to yield exclusively the 1:1 adduct [10].

Prompted by the results obtained with sulfonyl chlorides, we decided to investigate corresponding reactions with other S electrophiles, such as sulfenyl chlorides and sulfinyl chlorides. Whereas sulfinyl chlorides are relatively well-known and widely applied in organic synthesis [11a], sulfenyl chlorides are less well-known, and only a limited number of stable representatives are accessible [11b,c], including α-chlorosulfenyl chlorides, which only recently were prepared by chlorination of sterically crowded thioketones [12][13].

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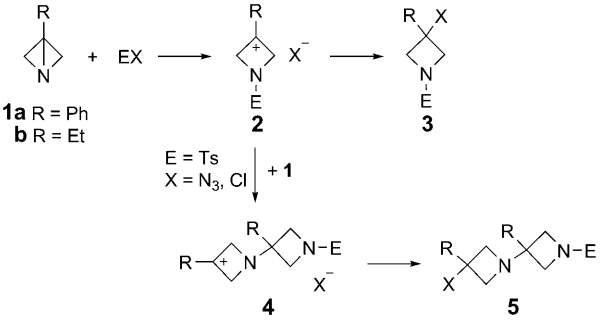
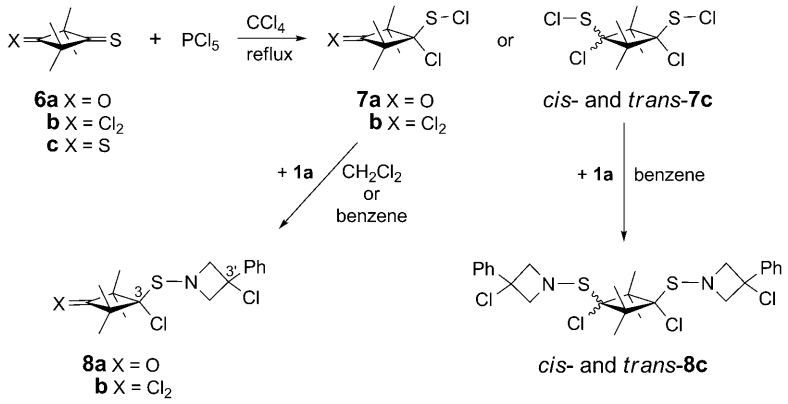
Scheme 1



Sulfinyl and sulfenyl chlorides are known to react with N-nucleophiles to yield sulfinamides and sulfenamides (sulfanyl-amines), respectively [11a,b][14]. They are formed *via* a substitution reaction in which HCl is eliminated. According to the reactions presented in *Scheme 1*, it could be expected that their reactions with **1** will lead, however, to azetidine derivatives of type **3**, which are 1,3-addition products. To the best of our knowledge, neither sulfinyl nor sulfanyl amides derived from azetidine have been reported to date. Sulfinamides are versatile building blocks [15] in asymmetric synthesis [16] and organocatalysis [17]. Furthermore, some of them have also invoked interest in medicinal chemistry [18][19]. In addition, in the case of sulfenamides, diverse applications are known, *e.g.*, in the rubber industry [20].

2. Results and Discussion. – 2.1. *Reactions with α-Chlorosulfenyl Chlorides.* Treatment of thioketones **6a** and **6b** with PCl_5 in boiling CCl_4 afforded α-chlorosulfenyl chlorides **7a** and **7b** [12][13], respectively, which, without further purification, were used for the reaction with **1a** in benzene or CH_2Cl_2 (*Scheme 2*). In the case of **6c**, the obtained mixture of nearly equal amounts of *cis*-**7c** and *trans*-**7c** was used without

Scheme 2



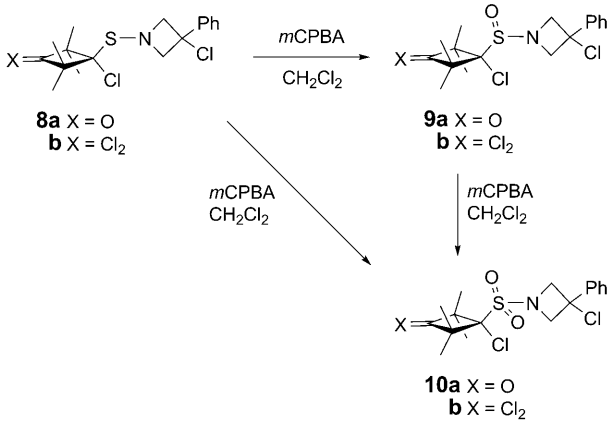
separation. The reactions with **1a** were carried out at *ca.* 5°, and, after 30 min, no starting materials could be detected by ^{1}H-NMR spectroscopy.

In the case of **7a**, the ^{1}H-NMR spectrum of the reaction mixture showed the presence of two sharp *singlet*s for Me groups at 1.30 and 1.37 ppm, as well as a broad *singlet* at 4.37 ppm, which can be attributed to the two CH_2 groups of the azetidine ring. The pure product was isolated as a crystalline material and identified as the sulfenamide **8a** (*Scheme 2*). The ^{13}C-NMR spectrum of **8a** showed, along with signals of Me groups (21.5 and 24.0 ppm) and CH_2 groups (74.7 ppm), signals for two quaternary C-atoms at 68.1 and 89.8 ppm, which were attributed to C(3) and C(3′). The C=O group absorbed at 217.3 ppm.

The analogous product **8b** was obtained from the reaction of **7b** and **1a**. For the reaction of *cis*/*trans*-**7c**, 2 mol-equiv. of **1a** were used, leading to the formation of a 1:2 adduct **8c** as a mixture of approximately equal amounts of the *cis*- and *trans*-isomers. The attempted separation of the diastereoisomers, either by crystallization or by preparative TLC, failed. As expected from the molecular symmetry, the ^{1}H-NMR spectrum of the *cis*-isomer showed two signals for Me groups at 1.40 and 1.58 ppm, whereas *trans*-**8c** is characterized by the presence of only one Me signal at 1.50 ppm. In contrast to the reaction of **1a** with TsN_3 [5], formation of biazetidine derivatives or oligomeric materials was not observed.

The crystalline sulfenamides **8a** and **8b** were sequentially oxidized by treatment with *meta*-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2 at room temperature. Using 1 mol-equiv. of *m*CPBA, they were smoothly converted into the corresponding sulfinamides **9a** and **9b**, respectively (*Scheme 3*).

Scheme 3



It is interesting to note that characteristic changes of the ^{1}H-NMR spectrum are observed when the conversion **8b** → **9b** occurs, *i.e.*, the four Me groups at the cyclobutane ring gave four signals at 1.40, 1.49, 1.67, and 1.82 ppm, and the CH_2 groups of the azetidine ring appeared as an *AB* system at 4.30 and 4.82 ppm (J_{AB} = 9.3 Hz) and a *singlet* at 4.45 ppm. This pattern indicates that the molecule of **9b**, in contrast to **8b**, does not possess a symmetry plane. In the IR spectrum (KBr), a strong absorption

band at 1112 cm^{-1} was attributed to the S=O group. In addition, the MS and elemental analyses evidenced **9b** as the mono-oxidation product of **8b**. Finally, crystallization from petroleum ether gave colorless crystals suitable for an X-ray crystal-structure determination, which established the proposed structure of **9b** (*Figure*).

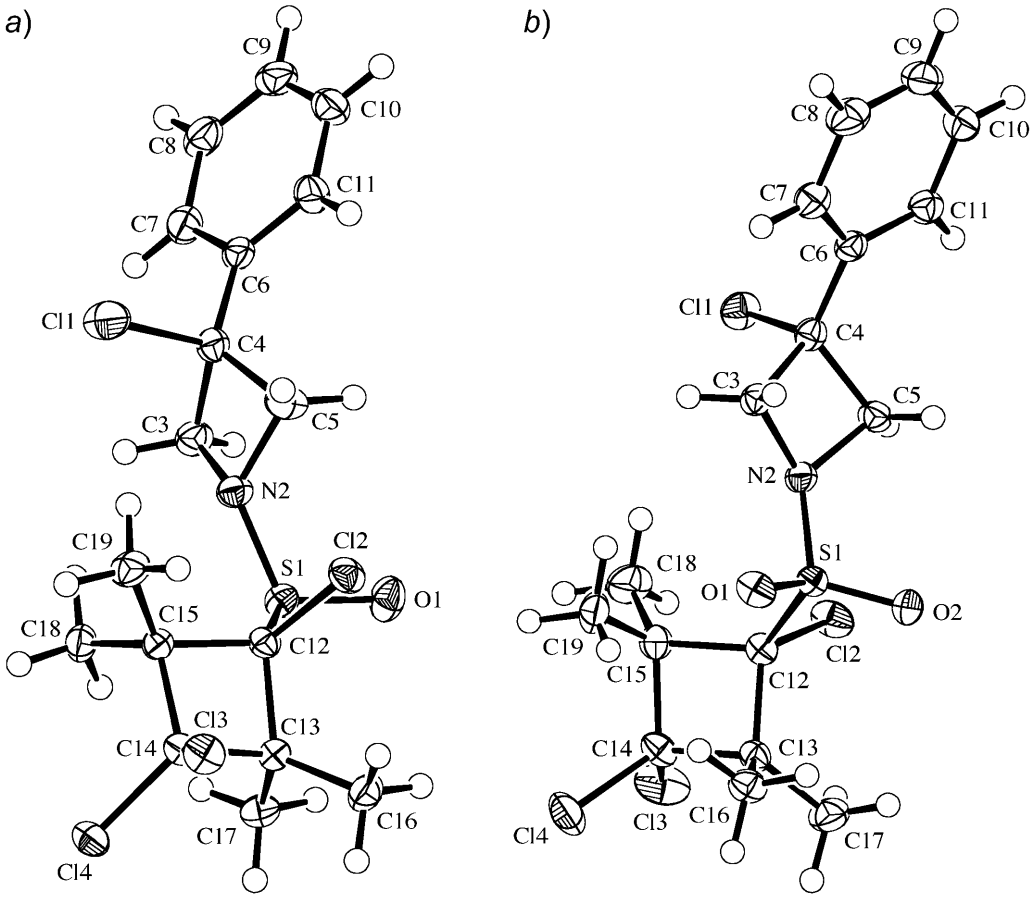


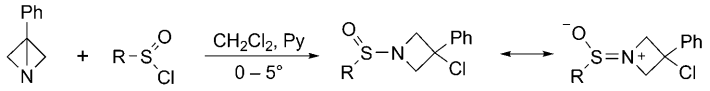
Figure. *ORTEP Plots* [21] *of the molecular structures of* a) **9b** *and* b) **10b** (arbitrary atom numbering; 50% probability ellipsoids)

Treatment of **8a** and **8b** with 2 mol-equiv. of *m*CPBA in CH_2Cl_2 gave, after longer reaction time at room temperature, the sulfonamides **10a** and **10b**, respectively. The ^{1}H-NMR spectra showed that the molecules are symmetric and, therefore, only two Me signals (1.55 and 1.75 mm for **10b**) and an *AB* system for two CH_2 groups (4.53 and 4.78 ppm, $J = 8.8$, for **10b**) were displayed. Two intense absorption bands at 1341 and 1156 cm^{-1} were in accordance with the values expected for sulfonamides [22]. Finally, the structure of **10b** was established by X-ray crystallography (*Figure*).

2.2. *Reactions with Sulfinyl Chlorides.* Sulfinyl chlorides **11a**–**11d**, which are easily accessible according to known protocols [23], were used for the reaction with 3-phenyl-

1-azabicyclo[1.1.0]butane (**1a**). The experiments were performed in CH_2Cl_2 at 0–5° in the presence of pyridine in order to avoid polymerization of **1a** induced by traces of HCl. After 1 h, the reactions were complete, and the ^{1}H-NMR spectra of the mixtures showed that **1a** was completely consumed. Instead of the two CH_2 *multiplet*s of **1a**, located at 1.50 and 2.77 ppm ($CDCl_3$), in all products, two *AB* systems appeared between 3.3 and 5.0 ppm. After chromatographic workup, sulfinamides **12** were obtained as crystalline materials, which are stable at room temperature (*Scheme 4*). Whereas the non-equivalency of the two CH_2 groups in **12a** was apparent only in the ^{1}H-NMR spectrum (*AB* systems at 4.47 and 4.66 ppm, $J_{AB} = 8.8$ and 9.9 Hz, resp.), the non-equivalency in the products **12b**–**12d** was also confirmed by the appearance of two CH_2 signals in the ^{13}C-NMR spectra (*e.g.*, for **12b**: 58.3 and 61.2 ppm).

Scheme 4



1a **11a** R = Me, **b** R = Et, **c** R = *t*-Bu, **d** R = Ph

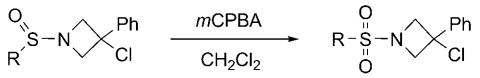
12a R = Me, **b** R = Et, **c** R = *t*-Bu, **d** R = Ph

It is worth mentioning that, in the ^{1}H-NMR spectra of sulfinamides obtained from **11c** and diethyl or dimethylamine, the *N*-alkyl groups are equivalent at room temperature [24][25]. Moreover, according to the studies of *Moriarty*, the rotation barrier in *N,N*-dimethylmethanesulfinamide is so low that even at −60° both MeN groups appear as a *singlet* [26]. These observations suggest that, in the series of new sulfinamides **12** derived from azetidines, the rotation barrier of the S–N bond is significantly higher, *i.e.*, the double-bond character of the S,N bond increases.

The S-atom of a sulfinamide is a stereogenic center and, therefore, sulfinamides are chiral compounds [15]. In a tentative experiment, a $CDCl_3$ solution of sulfinamide **12d** at room temperature was treated with an equimolar amount of (+)-(*R*)-(*tert*-butyl)(phenyl)thiophosphonic acid. The ^{1}H-NMR spectrum of this mixture showed that the low-field-shifted part of one *AB* system at 3.88 ppm has split into four lines with equal intensities within each part. This result confirmed the presence of two enantiomers of **12d** in the solution. Additional support came from the analytical HPLC experiment with a sample of racemic **12d** on a chiral solid phase (*Chiralpak AS*), in which two separated peaks with equal intensities were observed.

The isolated sulfinamides **12c** and **12d** were treated with *m*CPBA at room temperature to yield the expected sulfonamides **13a** and **13b**, respectively, in good yields (*Scheme 5*). As is characteristic for sulfonamides derived from azetidine (*e.g.*, **10a** and **10b**), the two CH_2 groups appear in the ^{1}H-NMR spectrum as an *AB* system between 4.3 and 4.8 ppm. In the ^{13}C-NMR spectrum, these groups appear as a single signal at 66.5 and 66.1 ppm for **13a** and **13b**, respectively. The characteristic strong bands for the sulfonamide group in the IR spectrum were found at 1315/1136 and 1352/1172 cm^{-1}, respectively.

Scheme 5



12c R = *t*-Bu
d R = Ph

13a R = *t*-Bu
b R = Ph

3. Conclusions. – The strained 3-phenyl-1-azabicyclo[1.1.0]butane (**1a**) reacts smoothly with sulfenyl and sulfinyl chlorides to give the expected sulfenamides and sulfinamides, respectively, with an azetidine residue. In contrast to similar reactions with sulfonyl chlorides, no oligomerization of **1a** was observed. As previously proposed for the addition reaction of EX with 1-azabicyclo[1.1.0]butanes (see *Scheme 1*), the reactions with sulfenyl chlorides **7** and sulfinyl chlorides **9** occur stepwise *via* the initial formation of an ion pair of type **2**. Subsequent addition of the Cl^- ion to the azetidinium ion leads to the final product. The ^{1}H-NMR analysis of the crude product mixture gave no indication for the competitive formation of a 2-azete derivative *via* deprotonation of the intermediate **2**.

The NMR data of the sulfinamides **12** clearly indicate that the rotation about the S–N bond in these compounds is much more hindered than in the known *N,N*-dialkyl-substituted analogues. Most likely, this is the result of the incorporation of the N-atom into a strained four-membered ring.

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Experimental Part

1. *General*. M.p.: in capillary with a *Meltemp 2* apparatus; uncorrected. IR Spectra: in KBr pellets with a *Nexus FT-IR* spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Tesla BS 687* (80 and 20 MHz, resp.) or *Bruker 300* spectrometer (300 and 75 MHz, resp.) with Me_4Si (=0 ppm) as internal standard; δ in ppm, J in Hz, the multiplicity of ^{13}C signals was determined by DEPT experiments. MS (EI or CI): *Finnigan Mat-90* or *Finnigan SSQ-700* spectrometer; CI with isobutane or NH_3; in m/z (rel. %). Elemental analyses were performed in the Analytical Laboratory of the University of Zürich and the Laboratory of the Polish Academy of Sciences (CBMiM) in Łódź.

2. *Starting Materials. 3-Phenyl-1-azabicyclo[1.1.0]butane* (**1a**) was prepared from trimethylsulfonium iodide, BuLi, and 3-phenyl-2*H*-azirine according to a known protocol [27]. *2,2,4,4-Tetramethyl-3-thioxocyclobutanone* (**6a**) [28], *3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione* (**6b**) [13], and *2,2,4,4-tetramethylcyclobutane-1,3-dithione* (**6c**) [29] were synthesized from 2,2,4,4-tetramethylcyclobutane-1,3-dione (for **6a** and **6c**) and 3,3-dichloro-2,2,4,4-tetramethylcyclobutanone (for **6b**) by thionation using P_2S_5 in pyridine soln. at 130°. *1-Chloro-2,2,4,4-tetramethyl-3-oxocyclobutanesulfenyl chloride* (**7a**) [12], *1,3,3-trichloro-2,2,4,4-tetramethylcyclobutanesulfenyl chloride* (**7b**) [13], and cis/trans-*1,3-dichloro-2,2,4,4-tetramethylcyclobutane-1,3-bis(sulfenyl chloride)* (*cis*/*trans*-**7c**) [12] were obtained from thioketones **6a**–**6c** by chlorination using PCl_5 in CCl_4 soln. according to known protocols. *Methanesulfinyl chloride* (**11a**), *ethanesulfinyl chloride* (**11b**), *2,2-dimethylethanesulfinyl chloride* (**11c**), and *benzenesulfinyl chloride* (**11d**) were synthesized according to literature protocols [23].

3. *Reactions of* **1a** *with α-Chlorosulfenyl Chlorides* **7a**–**7c**. *General Procedure.* To a magnetically stirred soln. of **7** (1 mmol) in 2 ml of benzene (**7a** and **7c**) or in 0.5 ml of CH_2Cl_2 (**7b**) at r.t., a soln. of **1a**

(131 mg, 1 mmol in the case of **7a** and **7b**, and 262 mg, 2 mmol in the case of **7c**) in benzene (1 ml) or CH_2Cl_2 (0.5 ml) was added, and stirring was continued for 30 min. Then, the solvent was evaporated, and the residue was washed with Et_2O, and filtered. The filtrate was evaporated to dryness, and the oily residue was crystallized from hexane (for **8a**) or Et_2O (for **8b**) after cooling the soln. in a dry ice box.

3-Chloro-3-[(3-chloro-3-phenylazetidin-1-yl)sulfanyl]-2,2,4,4-tetramethylcyclobutanone (**8a**). Yield: 259 mg (72%). Colorless crystals. M.p. 101–102° (hexane, −70°). IR (KBr): 3000*s*, 1780v*s* (C=O), 1450*s*, 1060*s*, 1020*s*, 715*s*, 695*s*. ^{1}H-NMR ($CDCl_3$): 1.30 (*s*, 2 Me); 1.37 (*s*, 2 Me); 4.37 (*s*, 2 CH_2); 7.13–7.43 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 21.6 (2 Me); 24.0 (2 Me); 63.7 (C_qCl); 68.1 (2 C_q); 74.7 (2 CH_2); 89.8 (C_qS); 125.7 (2 arom. CH); 128.5 (arom. CH); 129.1 (2 arom. CH); 142.5 (arom. C); 217.3 (C=O). EI-MS: 359 (18), 357 (26, $M^{+\cdot}$), 191 (57), 149 (93), 131 (100), 120 (79), 103 (63), 77 (58), 42 (56). Anal. calc. for $C_{17}H_{21}Cl_2NOS$ (358.33): C 56.98, H 5.91, N 3.91; found: C 56.62, H 5.95, N 4.04.

3-Chloro-3-phenyl-1-[(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl)sulfanyl]azetidine (**8b**). Yield: 80 mg (19%). Colorless crystals. M.p. 52–55° (Et_2O, −70°). IR (KBr): 3022*m*, 2941*m*, 2845*m*, 1471v*s*, 1447v*s*, 1072*m*, 871*s*, 833*s*, 823*m*, 804*s*, 758v*s*, 697v*s*, 619*s*. ^{1}H-NMR ($CDCl_3$): 1.46 (*s*, 2 Me); 1.54 (*s*, 2 Me); 4.39 (*s*, 2 CH_2); 7.29–7.46 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 25.1 (2 Me); 27.6 (2 Me); 58.9 (2 C_q); 63.5 (C_qCl); 74.4 (2 CH_2); 92.1 (C_qS); 98.8 (C_qCl_2); 125.4 (2 arom. CH); 128.2 (arom. CH); 128.7 (2 arom. CH); 142.2 (arom. C). CI-MS: 416 (17), 414 (34), 412 (26, $[M+1]^+$), 168 (10), 133 (11), 132 (100). Anal. calc. for $C_{17}H_{21}Cl_4NS$ (413.24): C 49.41, H 5.12, N 3.39, S 7.76; found: C 49.28, H 5.21, N 3.26, S 7.60.

cis/trans-*1,3-Dichloro-1,3-bis[(3-chloro-3-phenylazetidin-1-yl)sulfanyl]-2,2,4,4-tetramethylcyclobutane* (*cis*/*trans*-**8c**, ratio *ca.* 1:1). Yield: 422 mg (73%). Colorless oil; melts at r.t. after crystallization from pentane at −78°. IR (film): 2980*m*, 2960*m*, 2860*m*, 1440*s*, 1370*m*, 1310*m*, 1260*m*, 1160*m*, 1075*s*, 990*m*, 800*s*, 710*s*, 680v*s*. ^{1}H-NMR ($CDCl_3$): *cis*-**8**: 1.40 (*s*, 2 Me); 1.58 (*s*, 2 Me); 4.40 (br. *s*, 4 CH_2); 7.21–7.50 (*m*, 10 arom. H); *trans*-**8**: 1.50 (*s*, 4 Me); 4.40 (br. *s*, 4 CH_2); 7.21–7.50 (*m*, 10 arom. H). ^{13}C-NMR ($CDCl_3$): 23.6, 28.9 (4 Me, *cis*-**8c**); 26.4 (4 Me, *trans*-**8c**); 56.1, 56.6 (2 C_q, *cis*- and *trans*-**8c**); 63.8, 65.5 (2 C_qCl, *cis*- and *trans*-**8c**); 74.3, 74.4 (4 CH_2, *cis*- and *trans*-**8c**); 93.0, 93.8 (2 C_qS, *cis*- and *trans*-**8c**); 125.4 (4 arom. CH, *cis*- and *trans*-**8c**); 128.1 (2 arom. CH, *cis*- and *trans*-**8c**); 128.7 (4 arom. CH, *cis*- and *trans*-**8c**); 142.2 (2 arom. C_q, *cis*- and *trans*-**8c**). CI-MS (isobutane): 579 (2), 578 (3), 577 (3), 576 (4), 574 (3, $[M+1]^+$), 543 (8), 541 (14), 539 (13, $[M-Cl]^+$), 342 (74), 306 (100), 270 (34), 132 (42).

4. *Oxidation of* **8a** *and* **8b** *with* m*CPBA. General Procedure.* A magnetically stirred soln. of **8** (1 mmol) in CH_2Cl_2 (5 ml) was cooled in an ice-water bath, and a portion of *m*CPBA (1 mmol for the synthesis of **9a** and **9b**, or 6 mmol for the synthesis of **10a** and **10b**) was added in small portions. Stirring was continued for 15 min (for **9a** and **9b**) or 12 h (for **10a** and **10b**). Then, the soln. was diluted with CH_2Cl_2 (10 ml), and washed with a sat. aq. soln. of $NaHCO_3$, 2–5% NaOH, and brine. The org. layer was separated and dried, and the solvent was evaporated. Pure samples were obtained by crystallization from the appropriate solvent.

3-Chloro-3-[(3-chloro-3-phenylazetidin-1-yl)sulfinyl]-2,2,4,4-tetramethylcyclobutanone (**9a**). Yield: 230 mg (61%). Colorless crystals. M.p. 102–104° (petroleum ether). IR (KBr): 1794*s* (C=O), 1781*m*, 1105*s* (S=O), 1060*m*, 698*m*. ^{1}H-NMR ($CDCl_3$): 1.29, 1.37, 1.55, 1.70 (4*s*, 4 Me); 4.29, 4.90 (*AB*, $J_{AB}=9.3$, CH_2); 4.50 (*s*, CH_2); 7.34–7.48 (*m*, 5 arom. CH). ^{13}C-NMR ($CDCl_3$): 21.1, 21.7, 21.9, 22.1 (4 Me); 62.7, 64.5 (2 CH_2); 65.8 (C_qCl); 66.9, 67.1 (2 C_q); 91.7 (C_qS); 125.3 (2 arom. CH); 128.6 (arom. CH); 128.9 (2 arom. CH); 141.2 (arom. C); 214.7 (C=O). CI-MS (isobutane): 378 (12), 376 (65), 374 (100, $[M+1]^+$), 214 (10), 131 (13). Anal. calc. for $C_{17}H_{21}Cl_2NO_2S$ (374.33): C 54.55, H 5.65, N 3.74, S 8.57; found: C 54.62, H 5.87, N 3.78, S 8.61.

3-Chloro-3-phenyl-1-[(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl)sulfinyl]azetidine (**9b**). Yield: 179 mg (42%). Colorless crystals. M.p. 115–117° (petroleum ether). IR (KBr): 1449*m*, 1112*s* (S=O), 1080*m*, 1071*m*, 886*m*, 796*m*, 716*m*, 694*m*, 616*m*. ^{1}H-NMR ($CDCl_3$): 1.40, 1.49, 1.68, 1.82 (4*s*, 4 Me); 4.24, 4.84 (*AB*, $J_{AB}=9.4$, CH_2); 4.44 (*s*, CH_2); 7.32–7.38 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 24.6, 25.0, 25.1, 25.6 (4 Me); 57.6, 57.8 (2 C_q); 62.5, 64.4 (2 CH_2); 65.9 (C_qCl); 94.4 (C_qS); 98.0 (C_qCl_2); 125.3 (2 arom. CH); 128.6 (arom. CH); 128.8 (2 arom. CH); 141.2 (arom. C). CI-MS (isobutane): 434 (10), 432 (65), 430 (100), 428 (73, $[M+1]^+$). Anal. calc. for $C_{17}H_{21}Cl_4NOS$ (429.24): C 47.57, H 4.93, N 3.26, S 7.47; found: C 47.63, H 5.01, N 3.31, S 7.51.

3-Chloro-3-[(3-chloro-3-phenylazetidin-1-yl)sulfonyl]-2,2,4,4-tetramethylcyclobutanone (**10a**). Yield: 170 mg (44%). Colorless crystals. M.p. 94–98° (petroleum ether/CH_2Cl_2). IR (KBr): 1793*s*

(C=O), 1774*m*, 1337*s* (S=O), 1156*s* (S=O), 1115*m*, 719*m*, 655*m*, 632*m*, 618*m*. ^{1}H-NMR ($CDCl_3$): 1.49 (*s*, 2 Me); 1.62 (*s*, 2 Me); 4.59, 4.81 (*AB*, J_{AB} = 9.5, 2 CH_2); 7.36–7.44 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 20.6 (2 Me); 24.8 (2 Me); 61.4 (2 C_q); 67.3 (2 CH_2); 91.0 (C_qS); 125.3 (2 arom. CH); 128.9 (arom. CH); 129.0 (2 arom. CH); 140.7 (arom. C); 213.3 (C=O); signal for C_qCl missing. ^{13}C-NMR (C_6D_6): 21.4 (2 Me); 25.4 (2 Me); 62.6 (C_qCl); 67.8 (2 CH_2); 68.2 (2 C_q); 92.2 (C_qS); 126.2 (2 arom. CH); 129.0 (arom. CH); 129.7 (2 arom. CH); 141.7 (arom. C); 212.6 (C=O). CI-MS (isobutane): 392 (64), 390 (94, $[M+1]^+$), 354 (100, $[M-Cl]^+$), 131 (22). Anal. calc. for $C_{17}H_{21}Cl_2NO_3S$ (390.33): C 52.31, H 5.42, N 3.59, S 8.22; found: C 52.14, H 5.49, N 3.64, S 8.11.

3-Chloro-3-phenyl-1-[(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl)sulfonyl]azetidine (**10b**). Yield: 289 mg (65%). Colorless crystals. M.p. 119–121° (hexane/CH_2Cl_2). IR (KBr): 1341*s* (S=O), 1156*s* (S=O), 1112*m*, 695*m*, 663*s*, 622*m*. ^{1}H-NMR ($CDCl_3$): 1.55 (*s*, 2 Me); 1.75 (*s*, 2 Me); 4.53, 4.78 (*AB*, J_{AB} = 8.8, 2 CH_2); 7.40 (*s*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 25.3 (2 Me); 27.0 (2 Me); 58.3 (2 C_q); 61.3 (C_qCl); 67.3 (2 CH_2); 94.7 (C_qS); 97.7 (C_qCl_2); 125.3 (2 arom. CH); 128.8 (1 arom. CH); 129.0 (2 arom. CH); 140.7 (arom. C). ^{13}C-NMR (C_6D_6): 26.3 (2 Me); 27.6 (2 Me); 59.3 (2 C_q); 62.6 (C_qCl); 67.9 (2 CH_2); 95.7 (C_qS); 99.2 (CCl_2); 126.2 (2 arom. CH); 129.0 (arom. CH); 129.7 (2 arom. CH); 141.7 (arom. C). CI-MS (isobutane): 450 (4), 448 (19), 446 (37), 444 (27, $[M+1]^+$), 412 (45), 410 (100), 408 (85, $[M-Cl]^+$), 376 (48), 374 (62), 346 (37), 344 (39), 340 (26), 338 (28), 132 (38), 130 (67). Anal. calc. for $C_{17}H_{21}Cl_4NO_2S$ (445.24): C 45.86, H 4.75, N 3.15, S 7.20; found: C 45.79, H 4.83, N 3.09, S 7.10.

5. *Reactions of* **1a** *with Sulfinyl Chlorides* **11a**–**11d**. *General Procedure.* A magnetically stirred soln. of **11** (1 mmol) and dry pyridine (158 mg, 2 mmol) in CH_2Cl_2 (1 ml) was cooled in an ice-water bath, a soln. of **1a** (131 mg, 1 mmol) in CH_2Cl_2 (1 ml) was added in small portions, and stirring was continued for 1 h. Then, the soln. was diluted with CH_2Cl_2 (10 ml), washed with H_2O, and the org. layer was dried ($MgSO_4$). The solvent was evaporated, and pure products were obtained after prep. TLC (for **12a** and **12d**) or crystallization (for **12b** and **12c**).

3-Chloro-1-(methylsulfinyl)-3-phenylazetidine (**12a**). Yield: 100 mg (44%). Colorless crystals. M.p. 67–69° (Et_2O, −20°) IR (KBr): 1073*m* (br.), 1055*m*, 909*s*, 731*s*, 647*m*, 622*m*. ^{1}H-NMR ($CDCl_3$): 2.45 (*s*, Me); 4.14, 4.71 (*AB*, J_{AB} = 8.8, CH_2); 4.38 (*s*, CH_2); 7.30–7.52 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 38.9 (Me); 57.8, 60.7 (2 CH_2); 63.2 (C_qCl); 125.4 (2 arom. CH); 128.5 (arom. CH); 128.8 (2 arom. CH); 141.3 (arom. C). CI-MS (isobutane): 232 (34), 231 (11), 230 (100, $[M+1]^+$), 194 (16), 166 (18), 131 (29). Anal. calc. for $C_{10}H_{12}ClNOS$ (229.73): C 52.28, H 5.27, N 6.10, S 13.96; found: C 52.20, H 5.25, N 6.07, S 14.01.

3-Chloro-1-(ethylsulfinyl)-3-phenylazetidine (**12b**). Yield: 62 mg (25%). Colorless crystals. M.p. 71–72° (Et_2O, −20°). IR (KBr): 1075*s*, 1061*m*, 1052*m*, 1025*m*, 725*m*, 703*m*, 624*m*. ^{1}H-NMR ($CDCl_3$): 1.25 (*t*, *J* = 7.6, *Me*CH_2); 2.60 (*q*, *J* = 7.6, MeC*H*$_2$); 4.12, 4.72 (*AB*, J_{AB} = 8.5, CH_2); 4.40 (*s*, CH_2); 7.34–7.46 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 7.5 (*Me*CH_2); 46.7 (Me*C*H$_2$); 58.3, 61.2 (2 CH_2); 63.6 (C_qCl); 125.4 (2 arom. CH); 128.4 (arom. CH); 128.7 (2 arom. CH); 141.4 (arom. C). CI-MS: 246 (31), 244 (100, $[M+1]^+$). Anal. calc. for $C_{11}H_{14}ClNOS$ (243.76): C 54.20, H 5.79, N 5.75, S 13.16; found: C 54.27, H 5.65, N 5.68, S 13.49.

3-Chloro-1-[(1,1-dimethylethyl)sulfinyl]-3-phenylazetidine (**12c**). Yield: 170 mg (63%). Colorless crystals. M.p. 87–90° (Et_2O, −70°). IR (KBr): 2959*m*, 2928*m*, 1451*m*, 1363*m*, 1178*m* (br.), 1066v*s*, 1051*s*, 1021*m*, 728*s*, 705*m*, 621*m*. ^{1}H-NMR ($CDCl_3$): 1.19 (*s*, 3 Me); 4.10, 4.76 (*AB*, J_{AB} = 9.0, CH_2); 4.34, 4.48 (*AB*, J_{AB} = 8.8, CH_2); 7.30–7.46 (*m*, 5 arom. CH). ^{13}C-NMR ($CDCl_3$): 23.2 (3 Me); 57.4 (C_q); 61.6, 64.2 (2 CH_2); 64.9 (C_qCl); 125.4 (2 arom. CH); 128.3 (arom. CH); 128.7 (2 arom. CH); 141.8 (arom. C). CI-MS (NH_3): 291 (3), 289 (10, $[M+NH_4]^+$), 274 (35), 273 (15), 272 (100, $[M+1]^+$). Anal. calc. for $C_{13}H_{18}ClNOS$ (271.81): C 57.45, H 6.67, N 5.15, S 11.80; found: C 57.58, H 6.42, N 4.92, S 11.79.

3-Chloro-3-phenyl-1-(phenylsulfinyl)azetidine (**12d**). Yield: 185 mg (63%). Colorless thick oil. IR (film): 1444*m*, 1096*s*, 1075*m*, 1062*s*, 753*m*, 697*s*, 623*m*, 591*s*, 580*s*. ^{1}H-NMR ($CDCl_3$): 3.82, 4.56 (*AB*, J_{AB} = 8.8, CH_2); 4.30, 4.44 (*AB*, J_{AB} = 8.8, CH_2); 7.30–7.77 (*m*, 10 arom. H). ^{13}C-NMR ($CDCl_3$): 58.5, 60.6 (2 CH_2); 62.8 (C_qCl); 125.2 (2 arom. CH); 125.3 (2 arom. CH); 128.2 (arom. CH); 128.5 (2 arom. CH); 128.7 (2 arom. CH); 131.0 (arom. CH); 141.2, 142.0 (2 arom. C). CI-MS (isobutane): 294 (32), 293 (15), 292 (100, $[M+1]^+$), 132 (11), 131 (12). Anal. calc. for $C_{15}H_{14}ClNOS$ (291.80): C 61.74, H 4.84, N 4.80, S 10.99; found: C 61.85, H 4.95, N 4.72, S 10.83.

6. *Oxidation of* **12c** *and* **12d** *with* m*CPBA. General Procedure.* A magnetically stirred soln. of **12** (1 mmol) in CH_2Cl_2 (12 ml) was cooled in an ice-water bath, *m*CPBA (345 mg, 2 mmol) was added in small portions, and stirring was continued for 15 min. Then, the soln. was diluted with CH_2Cl_2 (10 ml), and washed with a sat. aq. soln. of $NaHCO_3$, 2% NaOH, and brine. The org. layer was separated, dried ($MgSO_4$), and the solvent was evaporated. Pure products were obtained after crystallization.

3-Chloro-1-[(1,1-dimethylethyl)sulfonyl]-3-phenylazetidine (**13a**). Yield: 183 mg (64%). Colorless crystals. M.p. 137–139° (hexane/CH_2Cl_2). IR (KBr): 1315*vs* (S=O), 1136*vs* (S=O), 1102*m*, 730*m*, 693*s*, 616*m*. ^{1}H-NMR ($CDCl_3$): 1.40 (*s*, 3 Me); 4.45, 4.68 (*AB*, J_{AB} = 10.1, 2 CH_2); 7.40 (*s*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 23.8 (3 Me); 60.1 (C_q); 61.5 (C_qCl); 66.5 (2 CH_2); 125.4 (2 arom. CH); 128.7 (arom. CH); 129.0 (2 arom. CH); 141.3 (arom. C). CI-MS (isobutane): 290 (19), 288 (58, $[M+1]^+$), 254 (12), 252 (100, $[M-Cl]^+$), 132 (37). Anal. calc. for $C_{13}H_{18}ClNO_2S$ (287.81): C 54.25, H 6.30, N 4.87, S 11.14; found: C 54.19, H 6.25, N 4.81, S 11.05.

Table. *Crystallographic Data for Compounds* **9b** *and* **10b**

	9b	**10b**
Crystallized from	petroleum ether	hexane/CH_2Cl_2
Empirical formula	$C_{17}H_{21}Cl_4NOS$	$C_{17}H_{21}Cl_4NO_2S$
Formula weight	429.23	445.23
Crystal color, habit	colorless, prism	colorless, plate
Crystal dimensions [mm]	$0.15 \times 0.15 \times 0.20$	$0.05 \times 0.08 \times 0.28$
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
Reflections for cell determination	71996	27149
2θ Range for cell determination [°]	4–55	4–55
Unit cell parameters		
a [Å]	13.5031(2)	7.3150(2)
b [Å]	6.2927(1)	13.1977(2)
c [Å]	23.1262(4)	20.9374(6)
β [°]	97.048(1)	98.439(1)
V [Å^3]	1950.21(5)	1999.44(9)
D_x [g cm^{-3}]	1.462	1.479
$\mu(MoK_\alpha)$ [mm^{-1}]	0.718	0.707
Scan type	ϕ and ω	ω
$2\theta_{(max)}$ [°]	55	55
Transmission factors [min; max]	0.849; 0.900	0.892; 0.968
Total reflections measured	42318	18106
Symmetry independent reflections	4425	4496
Reflections with $I > 2\sigma(I)$	3711	3518
Reflections used in refinement	4424	4496
Parameters refined; restraints	221	231
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0395	0.0359
$wR(F^2)$ (all data)	0.1005	0.0858
Weighting parameters [a; b][a])	0.0358; 2.5269	0.0347; 1.0875
Goodness-of-fit	1.103	1.028
Secondary extinction coefficient	–	0.0051(7)
Final Δ_{max}/σ	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.63; −0.56	0.37; −0.44

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

3-Chloro-3-phenyl-1-(phenylsulfonyl)azetidine (**13b**). Yield: 292 mg (95%). Colorless crystals. M.p. 87–90° (hexane/CH_2Cl_2). IR (KBr): 1448*m*, 1352v*s* (S=O), 1172v*s* (S=O), 1112*s*, 754*m*, 724*s*, 699*m*, 653*s*, 591*m*, 580*s*. ^{1}H-NMR ($CDCl_3$): 4.33, 4.51 (*AB*, J_{AB} = 9.6, 2 CH_2); 7.31–8.08 (*m*, 10 arom. H). ^{13}C-NMR ($CDCl_3$): 60.7 (C_qCl); 66.1 (2 CH_2); 125.2 (2 arom. CH); 128.3 (2 arom. CH); 128.7 (arom. CH); 128.8 (2 arom. CH); 129.3 (2 arom. CH); 133.7 (arom. CH); 133.8, 140.6 (2 arom. C). CI-MS: 310 (18), 308 (48, $[M+1]^+$), 274 (25), 272 (100, $[M-Cl]^+$). Anal. calc. for $C_{15}H_{14}ClNO_2S$ (307.80): C 58.53, H 4.58, N 4.55, S 10.42; found: C 58.21, H 4.69, N 4.53, S 10.35.

7. *X-Ray Crystal-Structure Determination of* **9b** *and* **10b** (*Table* and *Figure*)[2]). All measurements were performed on a *Nonius KappaCCD* diffractometer [30] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [31]. The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections based on the multi-scan method [32] were applied. Each structure was solved by direct methods using SIR92 [33], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the case of **10b**. In the case of **9b**, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. Neutral-atom scattering factors for non-H-atoms were taken from [34a], and the scattering factors for H-atoms were taken from [35]. Anomalous dispersion effects were included in F_c [36]; the values for f' and f'' were those of [34b]. The values of the mass attenuation coefficients are those of [34c]. All calculations were performed using the SHELXL97 [37] program.

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