Sulfonyl-Activated Cyclobutenes as Building Blocks for the Synthesis of Dihydrodiazepines[1]

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1,2-Bis(phenylthio)-1-cyclobutene (**5**), prepared in high yield using a modified literature procedure, was oxidized to the corresponding bis-sulfone **2**, sulfone-sulfoxide **9**, bis-sulfoxide **10**, or mono-sulfoxide **15** by means of hydrogen peroxide or sodium periodate, respectively. When treated with diazomethane the bis-sulfone **2** and the sulfone-sulfoxide **9** yield the dihydrodiazepines **4a** and **11**, respectively. The reactivity of these cyclobutenes and the regioselectivity of **9** is discussed in terms of the MNDO model.

Sulfonyl-aktivierte Cyclobutene als Synthesebausteine für die Synthese von Dihydrodiazepinen[1]

1,2-Bis(phenylthio)-1-cyclobuten (**5**), das nach einem modifizierten Literaturverfahren in hoher Ausbeute erhalten wurde, konnte mittels Wasserstoffperoxid bzw. Natriumperiodat zum entsprechenden Bis-sulfon **2**, Sulfon-sulfoxid **9**, Bis-sulfoxid **10** oder Mono-sulfoxid **15** oxidiert werden. Mit Diazomethan ergeben das Bis-sulfon **2** und das Sulfon-sulfoxid **9** die Dihydrodiazepine **4a** bzw. **11**. Die Reaktivität dieser Cyclobutene und die Regioselektivität von **9** werden im Rahmen des MNDO-Modells diskutiert.

Vinyl sulfoxides and vinyl sulfones are often used as dienophiles because of their high reactivity[2]. Further activation can be achieved with 1,2-bis(phenylsulfonyl)ethylenes[3]. Therefore, these olefins represent useful synthetic equivalents for acetylene[4]. The activating influence of the sulfonyl group also becomes noticeable in dipolar cycloadditions[5]. By inserting a sulfonyl group into the cyclobutene ring a considerable increase of the reactivity of the cyclobutene double bond is achieved. Thiete 1,1-dioxide (**1**) possesses excellent dienophilic[6] and dipolarophilic[7] properties. We showed that cycloadducts of cyclobutenes and 1,3-dipoles represent potential precursors to dihydroazepines[8] and dihydrodiazepines[9].

However, the ring enlargement of dipolar cycloadducts of thiete 1,1-dioxide (**1**) leading to seven-membered heterocycles has not succeeded yet. Either the adducts eliminate SO_2[7] or the cycloadduct of **1** reacts by splitting the SO_2-C bond[10].

According to our experience, keto groups in or methoxycarbonyl- and cyano groups at the four-membered ring favour the ring enlargement[8,9].

In order to examine how much the sulfonyl group facilitates the fission of the central σ bond of the cycloadducts of cyclobutenes (without competing cleavage of an outer bond of the four-membered ring), the preparation of bicyclic pyrazolines **3** with activating phenylsulfonyl substituents and their possible ring enlargement leading to **4** was investigated. We now report on the synthesis of 1,2-bis(phenylsulfonyl)-1-cyclobutene (**2**) and its reactivity towards diazoalkanes.

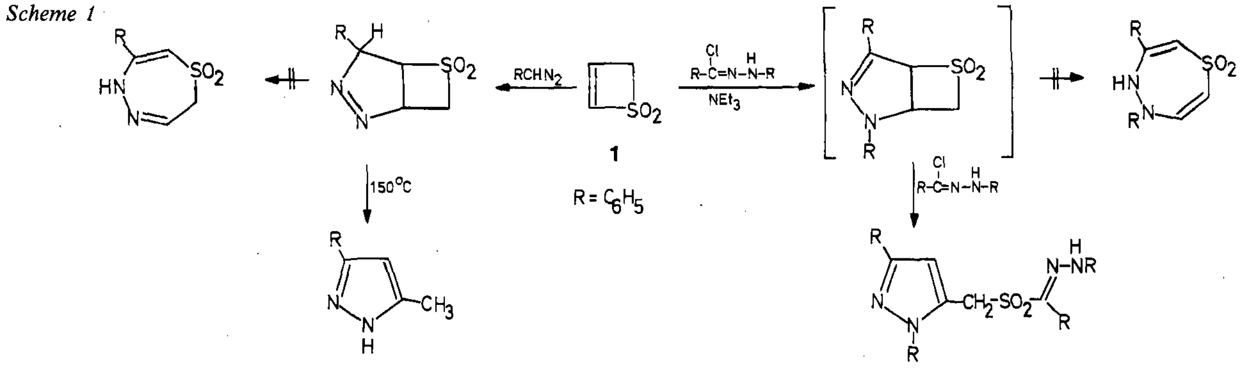
Results

The bis-sulfide **5**[11], described by Cohen et al., should be a suitable starting material for the sulfone **2**. However, the published yield of 70% for **5** could not be reproduced. With *sec*-butyllithium in THF at −78 °C mixtures of **5** and **8** were obtained (yields: ca. 50% of **5**, 30% of **8**).

We assume that **8** arises from 1,1-bis(phenylthio)ethylene (**7**) which originates from **6** by Grob fragmentation. The separation of **5** and **8** proved to be difficult. Fortunately, a variation of the experimental conditions (ether instead of THF) increased the yield of **5** to 85%, and undesired by-product **8** was no longer observed.

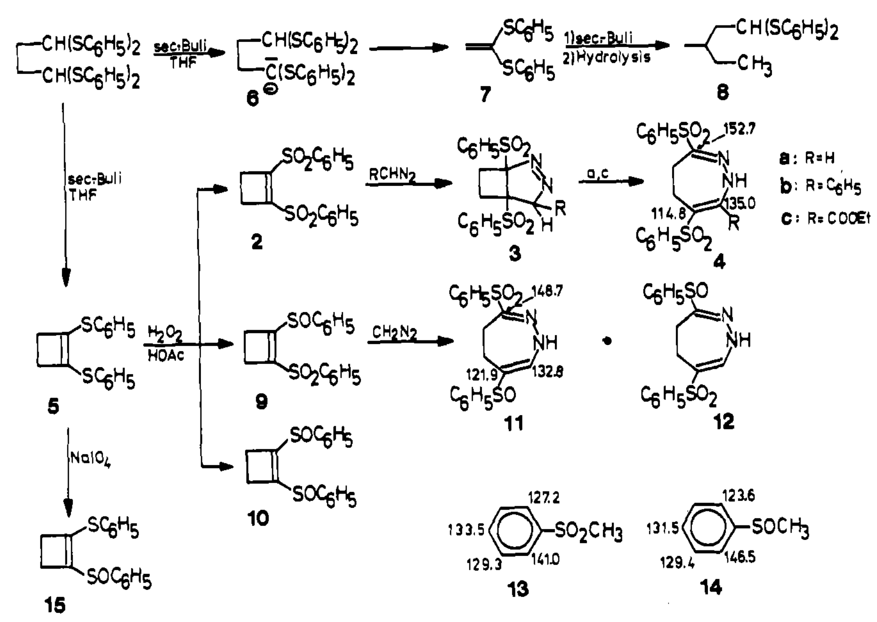
The oxidation of bis-sulfides leading to sulfide-sulfoxides, bis-sulfoxides, sulfide-sulfones, sulfoxide-sulfones, or bis-sulfones can be achieved with different oxidizing reagents

Scheme 1



Chem. Ber. 120, 171–175 (1987) 0009–2940/87/0202–0171 $ 02.50/0

Scheme 2



(H_2O_2, peracids, ozone, $NaIO_4$, $KMnO_4$)[12]. When the bis-sulfide **5** was treated with a solution of 30% H_2O_2 in glacial acetic acid (7.7 mmol of **5**/10 ml of 30% H_2O_2) the bis-sulfone **2** was isolated in a yield of 89%. A lower ratio of the reactants (3.7 mmol of **5**/1.2 ml of 30% H_2O_2) led to only 8% of **2**, but 51% of sulfoxide-sulfone **9** and 18% of bis-sulfoxide **10** were obtained by chromatography.

On TLC the analytically pure bis-sulfoxide **10** shows two spots lying close together, which indicate a mixture of the *meso*- and D,L-sulfoxides. The number and intensity of ^{13}C NMR signals allows us to conclude that the ratio of diastereomers is ca. 3:1.

Within a few hours the bis-sulfone **2** reacts with diazomethane to yield a colourless compound which proves to be the dihydrodiazepine **4a**. The bicyclic compound **3a** is not observed. On the other hand, with phenyldiazomethane the 1-pyrazoline **3b** is obtained. Ethyl diazoacetate reacts extraordinarily slowly, only after six weeks the adduct **4c** was isolated. So far neither acids (1 N HCl, CH_3CO_2H) nor bases (1 N NaOH, Et_3N) transformed the phenyldiazomethane adducts **3b** into the diazepine **4b**.

Reaction of the sulfoxide-sulfone **9** with diazomethane leads to a mixture of two components (ratio ca. 13:1) within a few hours. The structure **11** is assigned to the main product, whereas the by-product – characterized only by ^1H NMR – may be the regioisomer **12**.

The most significant evidence for the regiochemistry of **11** comes from the ^{13}C-NMR spectrum. The C-3 resonance of **4a** (C-3 δ = 152.7, C-6 114.8, C-7 135.0) compare very well with δ(C-3) of **11** (C-3 148.7, C-6 121.9, C-7 132.8) whereas C-6 is deshielded and C-7 shielded in **11**. This is characteristric for α- and β-C-atoms in sulfoxides and sulfones, resp. (cf. **13** and **14**[13]).

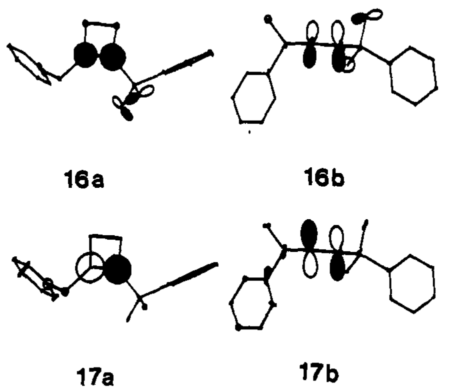
Oxidation of the bis-sulfide **5** with an equimolar amount of sodium periodate in methanol/water yields the sulfide-sulfoxide **15** as the main product.

Discussion

We will now investigate the reactivities of **2**, **5**, **9** and the regioselectivity of **9** in its reaction with diazomethane with the help of the MNDO model[14]. The most stable conformation for **5** in C_s symmetry bears the phenyl rings in an almost orthogonal position to the plane of the four-membered ring; the dihedral angle around the S – cyclobutene bond amounts to 21°.

Geometry optimization of the sulfoxide-sulfone **9** also furnishes phenyl groups distorted by ca. 90°. The dihedral angles around the SO_2 – cyclobutene and the SO – cyclobutene bond amount to 25 and 62°, respectively. The SO bond of the sulfoxide group deviates by 50° from the plane of the four-membered ring, the corresponding angles in the sulfone group amount to 143 and 94°, respectively. The π and π^* orbitals obtained for this structure are depicted in **16** and **17**.

Scheme 3


16a **16b**

17a **17b**

Table 1 records the energies and coefficients of those valence orbitals which show a dominating contribution to the CC double bond.

Table 1. Orbital energies (eV) and coefficients of the olefinic C-atom adjacent to S, SO, or SO_2 ($C_{S(O)}$, C_{SO_2}) according to MNDO. π and π* orbitals with a dominating contribution to the cyclobutene fragment. Geometry optimization **2** (C_{2v}), **5** (C_s), **9** (without restrictions), **10** (*meso*, C_s; D,L, C_2)

	ε	C_{SO_2}	$C_{S(O)}$	ε	C_{SO_2}	$C_{S(O)}$
2	−11.54	0.58	–	−1.01	0.68	–
5	−8.65	–	0.47	0.46	–	0.64
9	−11.21	0.56	0.52	−0.86	0.62	−0.65
10, *meso*	−10.74	–	0.57	−0.42	–	0.66
10, D,L	−10.73	–	0.52	−0.50	–	0.50

Table 2. Frontier molecular orbital data of diazomethane, phenyldiazomethane, and methyl diazoacetate (MNDO)

	ε/eV	C	N	N
CH_2N_2	+1.00	−0.58	+0.64	−0.51
	−8.67	−0.75	−0.18	+0.63
$C_6H_5CHN_2$	+0.06	−0.10	+0.19	−0.18
	−8.49	−0.70	−0.18	+0.58
MeO_2CCHN_2	−0.15	+0.37	−0.60	+0.53
	−9.34	−0.77	−0.14	+0.55

In Table 2 the energies of the frontier orbitals of the three diazoalkanes are given. The energy differences between the occupied and unoccupied orbitals of the reactants demonstrate that these cycloadditions are of type I, i.e. the unoccupied level of cyclobutene and the HOMO of the diazoalkane will control the reactivity and regioselectivity according to the frontier orbital model.

Only the bis-sulfide **5** which is inert towards diazomethane should add in a type II reaction. The increase of reactivity in the reactions with CH_2N_2 in the sequence $\mathbf{5} <<< \mathbf{2} \approx \mathbf{9}$ corresponds to the theoretically predicted lowering of the unoccupied π* level of cyclobutene ($0.46 > -1.01 \approx -0.86$). This result does indicate as well that the type I interaction is the dominating one. Accepting these facts one can also comprehend the high regioselectivity within the scope of the frontier orbital model and the MNDO calculations. The unoccupied molecular orbital **17** of the sulfoxide-sulfone **9** possesses a slightly larger coefficient on the sulfoxide side (cf. Table 1 and **17a, b**). In addition to that, the α-SO C-atom is sterically less shielded than the α-SO_2 C-atom. One of the SO bonds of the sulfone group is oriented almost parallel to the π bond of cyclobutene (Θ = 94) whereas the SO bond of the sulfoxide group is distorted towards the CH_2 units by 40° (thus, the dihedral angle with the plane of the four-membered ring amounts to 50°, cf. **16b**). The favoured attack of the nucleophilic and sterically more demanding C-atom of diazomethane on the C-atom α to SO is thus made plausible.

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Experimental

All melting and boiling points are uncorrected. – NMR spectrometer: Varian EM 360, XL-100. – Mass spectrometer: Varian MAT CH-5. – UV spectrometer: ZEISS M4-QIII.

1,2-Bis(phenylthio)-1-cyclobutene (**5**): 1,1,4,4-Tetrakis(phenylthio)butane[11] (25.0 g, 51.0 mmol) and *N,N,N',N'*-Tetramethylethylenediamine (25 ml, 166 mmol) are solved in 1.4 l of dry ether. Under nitrogen 120 ml of *sec*-butyllithium (1.3 M in cyclohexane) is slowly added with vigorous stirring at −70°C. The solution turns yellow. After 30 min at −70°C the solution is allowed to come to 0°C and after 1 h it is hydrolyzed with 20% NaOH. The ether solution is dried over $MgSO_4$ and the product is purified by flash chromatography[15] (silica gel 60; 230–400 mesh ASTM, Macherey & Nagel, eluent hexane). Yield 11.8 g (85%), m.p. 28°C (ref.[11] yellow oil). – UV (methanol): λ_{max} (lg ε) = 277 (4.35), 255 nm (4.32). – ^1H NMR (60 MHz, $CDCl_3$): δ = 2.55 (s; 4H, CH_2), 7.2 (mc; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 31.4 (t; C-3,4), 126.8 (d; phenyl, *p*-C), 128.6 (d; phenyl, *m*-C), 131.0 (d; phenyl, *o*-C), 132.4 and 135.3 (s; phenyl, *i*-C or C-1,2).

3-Methyl-1,1-bis(phenylthio)pentane (**8**): Preparation as given for **5** but using 650 ml of THF instead of ether. Hydrolysis with a cold solution of ammonium chloride. The crude product is separated by column chromatography. Yield 7.10 g of **5** (51%), 5.10 g of **8** (33%), yellow oil. – ^1H NMR (60 MHz, $CDCl_3$): δ = 0.8–2.7 (m; 11H, CH, CH_2, CH_3), 4.5 (t; 1H, CHS), 7.5 (mc; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 10.9 (q; C-5), 18.7 (q; C-6), 28.9 (t; C-4), 31.9 (d; C-3), 42.7 (t; C-2), 56.4 (d; C-1), 127.3 (d; phenyl, *p*-C), 128.5 (d; phenyl, *m*-C), 132.4, 132.6 (d; phenyl, *o*-C), 133.8, 134.1 (s; phenyl, *i*-C). – MS (70 eV): *m/z* = 302 (2%, M^+), 218 (18, $(C_6H_5S)_2^+$), 123 (66, $C_6H_5SCH_2^+$).

1,2-Bis(phenylsulfonyl)-1-cyclobutene (**2**): 2.10 g (7.77 mmol) of **5** is solved in 20 ml of glacial acetic acid. At room temp. 10 ml of a solution of H_2O_2 (30%) in 20 ml glacial acetic acid is added dropwise. After 3 h at 60°C 20 ml of water is added. The residue is suction-filtered, washed with water, and dried: 2.22 g, m.p. 134–135°C. After removing excess H_2O_2 with sodium hydrogen sulfite, concentrating, neutralising with sodium carbonate, and extracting with dichloromethane further 100 mg of **2** can be isolated from the filtrate. Yield 2.32 g (89%), m.p. 134–135°C. – IR (KBr): 3060 (CH), 2940 (CH_2), 1580 (C=C), 1440 cm^{-1} (CH_2). – UV (Methanol): λ_{max} (lg ε) = 248 nm (3.94). – ^1H NMR (60 MHz, $CDCl_3$): δ = 2.72 (s; 4H, CH_2), 7.5–8.2 (m; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.2 (t; C-3,4), 128.6 (d; phenyl, *o*-C), 129.2 (d; phenyl, *m*-C), 134.4 (d; phenyl, *p*-C), 138.0 (s; phenyl, *i*-C), 147.4 (s; C-1,2). – MS (70 eV): *m/z* = 334 (11%, M^+), 125 (100, $C_6H_5SO^+$).

$C_{16}H_{14}O_4S_2$ (334.4)	Calcd.	C 57.47	H 4.22	S 19.18
	Found	C 57.31	H 4.20	S 19.14

1-(Phenylsulfinyl)-2-(phenylsulfonyl)-1-cyclobutene (**9**) *and 1,2-Bis(phenylsulfinyl)-1-cyclobutene* (**10**): A solution of 1.25 ml of H_2O_2 (30%) in 2 ml of glacial acetic acid is added dropwise to a solution of **5** (1.00 g, 3.70 mmol) in 8 ml of glacial acetic acid. After 3 h at 60°C white crystals are formed on cooling. 50 ml of water is added, the precipitate is filtered, washed with water, and dried in vacuo. The three components of the crude product are separated by flash chromatography (silica gel 60, Macherey & Nagel, eluent hexane/ethyl acetate 1:5). Yields 0.10 g (8%) of **2**, m.p. 134–135°C, 0.60 g (51%) of **9**, m.p. 107–109°C, 0.21 g (18%) of **10**, m.p. 113.5 bis 114.5°C.

UV (Methanol), **9**: λ_{max} (lg ε) = 242 nm (4.24). **10**: λ_{max} = 235 nm (4.29). – ^1H NMR (60 MHz, $CDCl_3$): δ = 2.6 (mc; 4H, CH_2), 7.5 – 8.2 (m; 10H, aromatic H), **10**: δ = 2.6 (m; 4H, CH_2), 7.6 (m; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$), **9**: δ = 24.6, 27.7 (t; C-3,4), 124.2 (d; SO – phenyl, *o*-C), 127.9 (d; SO_2 – phenyl, *o*-C), 129.3, 129.4 (d; phenyl, *m*-C), 131.3 (d; SO – phenyl, *p*-C), 134.2 (d; SO_2 – phenyl, *p*-C), 137.8 (s; SO_2 – phenyl, *i*-C), 141.2 (s; SO – phenyl, *i*-C), 143.9, 155.7 (s; C-1,2), **10** (mixture of *meso* and D,L: δ = 26.0, 26.1 (t; C-3,4), 124.5, 124.6 (d; phenyl, *o*-C), 129.3, 129.4 (d; phenyl, *m*-C), 131.2, 131.3 (d; phenyl, *p*-C), 141.5_1, 141.5_3 (s; phenyl, *i*-C), 150.5, 150.9 (s; C-1,2). – MS (70 eV), **9**: *m/z* = 318 (6%, M^+), 177 (70, M – $C_6H_5SO_2$), 77 (100, $C_6H_5^+$), **10**: *m/z* = 302 (18%, M^+), 177 (90, M – C_6H_5SO), 128 (100, M – $C_6H_5S_2O_2H$), 77 (96, C_6H_5).

$C_{16}H_{14}O_3S_2$ (318.4) Calcd. C 60.35 H 4.43 S 20.14
Found C 60.21 H 4.34 S 20.10
$C_{16}H_{14}O_2S_2$ (302.4) Calcd. C 63.55 H 4.67 S 21.21
Found C 63.60 H 4.72 S 21.09

1-(Phenylsulfinyl)-2-(phenylthio)-1-cyclobutene (**15**): At –25°C a solution of sodium periodate (0.79 g, 3.69 mmol) in 8 ml water is added dropwise to a solution of **5** (1.00 g, 3.70 mmol) in 50 ml of methanol. After stirring for 10 h at room temp. the precipitate is filtered and washed with chloroform (3 × 10 ml). After removing the solvent under reduced pressure the product is purified by chromatography using silica gel. With dichloromethane 100 mg of **5** are eluted, the oxides are obtained with hexane/ethylacetate (1:2). Yields 650 mg (61%) of **15** (oil), 100 mg (10%) of **10**. – UV (methanol): λ_{max} (lg ε) = 276 (3.97), 269 (3.98), 261 (3.98), 218 nm (4.06). – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 2.1 – 2.9 (m; 4H, CH_2), 7.2 – 7.6 (m; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 25.0 (t; C – H), 31.0 (t; C-3), 124.0 (d; SO – phenyl, *o*-C), 128.9 (d; S – phenyl, *m*-C), 129.0 (s; S – phenyl, *i*-C), 129.0 (d; S – phenyl, *p*-C), 129.2 (d; SO – phenyl, *m*-C), 130.3 (d; SO – phenyl, *p*-C), 133.7 (d; S – phenyl, *o*-C), 136.0, 148.3 (s; C-1,2), 142.2 (s; SO – phenyl, *i*-C). – MS (70 eV): *m/z* = 286 (3%, M^+), 238 (100, M – SO).

$C_{16}H_{14}OS_2$ (286.4) Calcd. C 67.10 H 4.93 S 22.39
Found C 66.83 H 4.92 S 22.12

4,5-Dihydro-3,6-bis(phenylsulfonyl)-1H-1,2-diazepine (**4a**): 40 ml of a solution of diazomethane in ether (ca. 0.3 M) is added to 1.00 g of **2** (2.99 mmol). The mixture is stirred for 2 d in the dark. The colourless crystals are suction-filtered and washed with cold pentane. Purification by means of flash chromatography (silica gel, hexane/ethyl acetate 1:5). Yield 0.91 g (80%), m.p. 215 – 216°C. – IR (KBr): 3300 (NH), 1640 (C=N), 1580 (C=C), 1490 cm^{-1} (C=C). – UV (methanol): λ_{max} (lg ε) = 317 (4.12), 273 (3.28), 266 (3.38), 258 (3.50), 217 nm (4.14). – ^{1}H NMR (60 MHz, [D_6]-DMSO): δ = 2.3 – 3.1 (AA'BB'-m; 4H, CH_2), 7.4 (d; *J* = 5 Hz; 1H, olefinic), 7.5 – 8.1 (m; 10H, aromatic H), 11.0 (d, *J* = 5 Hz; 1H, NH). – ^{13}C NMR ([D_6]DMSO): δ = 26.2 (t; C-5), 28.0 (t; C-4), 114.8 (s; C-6), 126.8, 128.1 (d; phenyl, *o*-C), 129.2 (d; phenyl, *m*-C), 132.7, 133.8 (d; phenyl, *p*-C), 135.0 (d; C-7), 137.3, 139.7 (s; phenyl, *i*-C), 152.7 (s; C-3). – MS (70 eV): *m/z* = 376 (14%, M^+), 235 (21, M – $C_6H_5SO_2$), 77 (100, $C_6H_5^+$).

$C_{17}H_{16}N_2O_4S_2$ (376.4) Calcd. C 54.24 H 4.28 N 7.44 S 17.03
Found C 54.24 H 4.34 N 7.47 S 16.94

4-Phenyl-1,5-bis(phenylsulfonyl)-2,3-diazabicyclo[3.2.0]hept-2-ene (**3b**): A solution of phenyldiazomethane in pentane (ca. 0.3 M) is added dropwise to a solution of 1.50 g of **2** (4.49 mmol) in 30 ml of ethyl acetate. After 10 h the colourless crystals are filtered and washed with cold pentane. The crude product is dissolved in dichloromethane and precipitated with pentane. Yield 1.80 g (89%), m.p. 154 – 155°C (decomp.). – UV (methanol): λ_{max} (lg ε) = 273 (2.95), 265 (3.03), 259 (2.98), 217 nm (4.11). – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 1.75 (m; 2H, CH_2), 3.0 (m; 2H, CH_2), 6.6 (m; 3H, 4-H, *C*-phenyl, *o*-H), 7.2 (m; 3H, *C*-phenyl, *m,p*-H), 7.5 – 8.2 (m; 10H, SO_2 – phenyl). – ^{13}C NMR ($CDCl_3$): δ = 21.4, 26.4 (t; C-6,7), 71.0 (s; C-5), 97.3 (d; C-4), 112.0 (s; C-1), 127.4 (d; *C*-phenyl, *o*-C), 128.4 (d; *C*-phenyl, *m*-C), 128.7_0 (d; SO_2 – phenyl, *m*-C), 128.7_8 (d; *C*-phenyl, *p*-C), 129.2 (d; SO_2 – phenyl, *m*-C), 129.9, 130.7_2 (d; SO_2 – phenyl, *o*-C), 130.7_9 (s; *C*-phenyl, *i*-C), 134.5 (d; SO_2 – phenyl, *p*-C), 136.8, 137.2 (s; SO_2 – phenyl, *i*-C). – MS (70 eV): *m/z* = 424 (2%, M – N_2), 283 (98, M – (N_2 + $C_6H_5SO_2$)), 125 (100, $C_6H_5SO^+$).

$C_{23}H_{20}N_2O_4S_2$ (452.5) Calcd. C 61.04 H 4.45 N 6.19 S 14.17
Found C 60.90 H 4.53 N 6.20 S 14.05

Ethyl 4,5-Dihydro-3,6-bis(phenylsulfonyl)-1H-1,2-diazepine-7-carboxylate (**4c**): 2.1 g (18.4 mmol) of ethyl diazoacetate is added to 1.0 g (3.0 mmol) of **2**. After 2 weeks the sulfone has dissolved and after further 4 weeks the excess of ethyl diazoacetate is removed by chromatography (hexane/ethyl acetate 2:1). The product is eluted with hexane/ethyl acetate (1:3). It is dissolved in ethyl acetate and precipitated with pentane. Colourless crystals are obtained, yield 1.1 g (82%), m.p. 121 – 122.5°C. – IR (KBr): 3300 (NH), 1730 (C=O), 1640 cm^{-1} (C=C). – UV (methanol): λ_{max} (lg ε) = 316 (4.19), 273 (3.47), 265 (3.56), 258 (3.63), 252 (3.69), 219 nm (4.26). – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 1.30 (t; 3H, CH_3), 2.6 (mc; 4H, CH_2), 4.40 (q; 2H, OCH_2), 7.4 – 8.0 (m; 10H, aromatic H), 9.6 (s; 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 13.5 (q; CH_3), 26.8 (t; C-5), 30.0 (t; C-4), 63.3 (t; OCH_2), 116.8 (s; C-6), 127.5, 128.4 (d; phenyl, *o*-C), 129.0, 129.3 (d; phenyl, *m*-C), 133.2, 134.0 (d; phenyl, *p*-C), 136.9, 139.3 (s; phenyl, *i*-C), 141.3 (s; C-7), 150.1 (s; C-3), 162.2 (s; CO). – MS (70 eV): *m/z* = 448 (3%, M^+), 77 (100, $C_6H_5^+$).

$C_{20}H_{20}N_2O_6S_2$ (448.5) Calcd. C 53.56 H 4.49 N 6.25 S 14.30
Found C 53.51 H 4.50 N 6.15 S 14.25

4,5-Dihydro-6-(phenylsulfinyl)-3-(phenylsulfonyl)-1H-1,2-diazepine (**11**): 70 ml of a solution of diazomethane in ether (ca. 0.3 M) is added dropwise to **9** (0.96 g, 3.01 mmol) in 20 ml of ethyl acetate. After 10 h the solvent is removed, the residue dissolved in dichloromethane and precipitated with ether. The crude product is purified by chromatography (hexane/ethyl acetate 1:5). Two products (ratio 13:1) are obtained. The by-product (presumably **12**) did not crystallize so far. Yield 0.65 g (60%) of **11**, m.p. 162 – 164°C (decomp.), 0.05 g (5%) of **12**.

11: IR (KBr): 3300 (NH), 1640 (C=N), 1580 (C=C), 1480 cm^{-1} (C=C). – UV (methanol): λ_{max} (lg ε) = 316 (3.98), 273 (3.17), 266 (3.19), 259 (3.56), 218 nm (4.08). – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 2.45 (mc; 4H, CH_2), 7.25 (d; *J* = 5 Hz; 1H, olefinic), 7.8 (mc; 10H, aromatic H), 10.33 (d, *J* = 5 Hz; 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 23.0 (t; C-5), 29.7 (t; C-4), 121.9 (s; C-6), 124.3 (d; SO – phenyl, *o*-C), 128.0 (d; SO_2 – phenyl, *o*-C), 128.9 (d; SO – phenyl, *m*-C), 129.3 (d; SO_2 – phenyl, *m*-C), 130.4 (d; SO – phenyl, *p*-C), 132.8 (d; C-7), 133.8 (d; SO_2 – phenyl, *p*-C), 137.4 (s; SO_2 – phenyl, *i*-C), 148.8 (s; SO – phenyl, *i*-C), 148.7 (s; C-3). – MS (70 eV): *m/z* = 360 (0.2%, M^+), 344 (4, M – O), 109 (45, $C_6H_5S^+$), 77 (100, $C_6H_5^+$).

$C_{17}H_{16}N_2O_3S_2$ (360.4) Calcd. C 56.65 H 4.47 N 7.77 S 17.79
Found C 56.70 H 4.47 N 7.59 S 17.48

12: ^{1}H NMR (60 MHz, $CDCl_3$): δ = 2.3 (mc; 4H, CH_2), 7.4 – 7.9 (m; 11H, aromatic H, olefinic H), 9.15 (d; *J* = 5 Hz; 1H, NH).

CAS Registry Numbers

2: 105858-77-3 / **3b**: 105858-82-0 / **4a**: 105882-01-7 / **4c**: 105858-83-1 / **5**: 70871-28-2 / **8**: 105858-76-2 / **9**: 105858-78-4 / (*meso*)-**10**: 105858-79-5 / (*D,L*)-**10**: 105858-80-8 / **11**: 105858-84-2 / **12**: 105858-85-3 / **15**: 105858-81-9 / $(PhS)_2CH(CH_2)_2CH(PhS)_2$: 53480-95-8 / $EtO_2CCH{=}N_2$: 623-73-4

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[154/86]