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Regioselectivity of Oxysulfenylations of Cycloocta-1,5-diene

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Abstract. The regioselectivity of transannular *O*-heterocyclization of cycloocta-1,5-diene (**1**) with phenylsulfenyl chloride and methanol or water, respectively, is determined by the oxy-component which acts as nucleophilic partner in the electrophilic three component reaction. The thermodynamically more stable *endo,endo*-2,6-bis(phenylsulfenyl)-9-oxabicyclo[3.3.1]nonane (**2**) is formed almost exclusively in methanol while the isomeric 9-oxabicyclo[4.2.1]nonane (**3**) is favored under kinetic control in the presence of water. The oxidation of **2** or **3** yields the bissulfones **4** and **5**, respectively.

Continuing our investigations on transannular heterocyclizations sulfenylation reactions of cycloocta-1,5-diene (**1**) in the presence of oxygen nucleophiles became interesting in order to get 9-oxabicyclic bis-thioethers in a three component reaction [1].

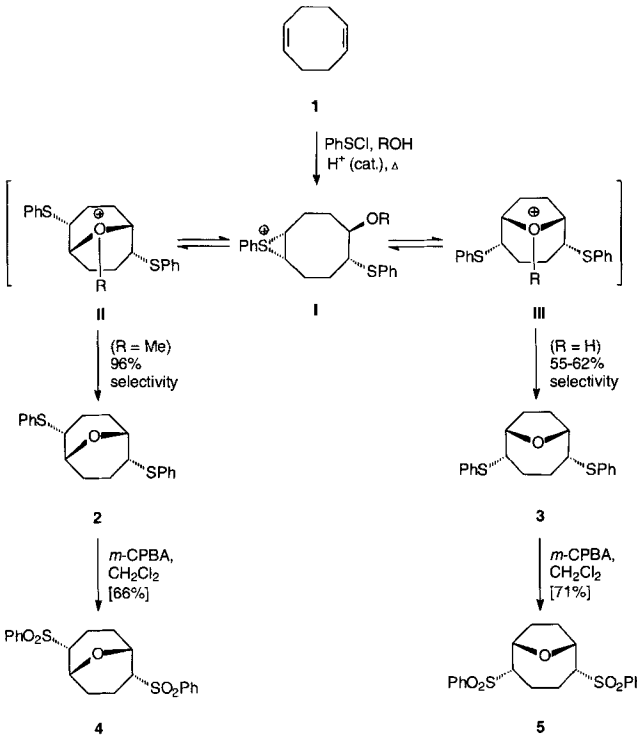
Several years ago two research groups investigated phenylselenenylations of diene **1**. Nicolaou *et al.* got high yield of *endo,endo*-2,5-bis(phenylselenenyl)-9-oxabicyclo[4.2.1]nonane by treatment of **1** with diphenyldiselenide [2] in the presence of water, or even better using *N*-phenylselenenyl phthalimide or *N*-phenylselenenyl succinimide [3] as the reagent donating the electrophile. On the other hand Uemura *et al.* obtained a strong solvent dependence in reactions of **1** with phenylselenenyl chloride [4] or phenylselenenyl cyanate/copper(II)-chloride [5] in different alcohols or in the presence of water, to give mixtures of the above-mentioned compound and its isomer *endo,endo*-2,6-bis(phenylselenenyl)-9-oxabicyclo[3.3.1]nonane. Since such a solvent dependence was not noticed before [6] this result was discussed to be a curiosity of organoselenium chemistry [5a]. Later on it became obvious, that this type of regioselectivity is caused both by bridging ability of the electrophile and by the nucleophilic partner, and hence by the quality of the leaving group which is released from intermediate oxonium ions [7].

This study presents our results on oxysulfenylation of **1**. Neither treatment of cycloocta-1,5-diene (**1**) with *N*-phenylsulfenyl phthalimide nor with *N*-phenylsulfenyl succinimide in water gave any reaction, possibly because of the stability of the nitrogen–sulfur bond. Synthesis of *endo,endo*-2,6-bis(phenylsulfenyl)-9-oxabicyclo[3.3.1]nonane (**2**) and *endo,endo*-2,5-bis(phenylsulfenyl)-9-oxabicyclo[4.2.1]nonane (**3**), however can be established by reaction of **1** with phenylsulfenyl chloride in acidic protic solution. Maybe phenylsulfenic acid is formed as an intermediate [8]. The ratio of the thermodynamically more stable (3.5 kcal/mol, AM1) bicyclic ether **2** and the kinetically favored **3** depends on the solvent used which is the nucleophilic partner in the three component addition [1] (Scheme 1, Table 1). The two isomers can be separated by column chromatography with cyclohexane : ethyl acetate 10 : 1 to give pure isomers. A rearrangement of **3** to the more stable isomer **2** is neither observed by refluxing in toluene nor in ethanol under acidic conditions.

The formation of the two isomers can be explained by the nature of the intermediates. After hydroxy- or methoxy-phenylsulfenylation of the first double bond one more attack of another molecule of the electrophile on the other double bond takes place and intermediate **I** is formed (Scheme 1). A transannular attack of the oxygen function on the carbocationic centers at the other side of the ring follows. The transannular cyclizations **I**→**II** and **I**→**III** of the bridged episulfonium ion **I** bearing the charge mainly on the sulfur are reversible. However, the formation of **III** is favored kinetically [6a, 9]. If R is a poor leaving group like methyl in the case of methanol as the nucleophile, the intermediate **III** is isomerized to the thermodynamically more stable oxonium ion **II**, from which the ether **2** is formed as main product.

In contrast, when R is a good leaving group like a proton, **III** is deprotonated faster than rearranged to

[1] X-Ray analysis



Scheme 1

Tab. 1 Results of *O*-heterocyclizations of cycloocta-1,5-diene (**1**)

Solvent	Time (h)	Yield (%) [a]	Ratio **2** : **3**
MeOH	24	48	96 : 4
THF : H_2O 24 : 1	24	45	45 : 55
MeCN : H_2O 5 : 1	24	53	38 : 62

[a] combined yield of compounds **2** and **3**

II, hence the kinetically favored ether **3** is formed dominantly. The differing influence of the co-solvents THF and acetonitrile could be due to different stabilization of the intermediates.

The configuration and the conformation in crystalline state of **2** and **3** become obvious from X-ray analysis. The X-ray structure of **3** [10] and that of **2** (Figure 1) [11] show the *endo,endo*-configuration of the two substituents. The chair conformation of the six-membered rings is clearly perceptible.

The orientation of both phenyl rings in vertical position to the level of the bicyclus is nearly the same because of disposal interactions in the crystal. This compound crystallizes in an orthorombic crystal system, space group Pbcn.

Next our attention turned on the selective oxidation of compounds **2** and **3** in order to synthesize the corresponding bissulfoxides. These compounds should give better excess to the corresponding 9-oxabicyclononadienes by thermal *syn*-elimination compared to *anti*-elimination of the corresponding *endo,endo*-dihalo-9-oxabicyclononanes described earlier [6b, 6c, 6f]. It is well known that bissulfoxides are difficult to synthesize. Consequently, in numerous experiments with different amounts of *meta*-chloroperbenzoic acid (*m*-CPBA) under modified reaction conditions no selective oxidation was achieved. Always mixtures of bissulfones, sulfonosulfoxides, bissulfoxides and sulfoxidosulfides were formed which were difficult to separate by column chromatography or crystallization, respectively. In contrast, the oxidation of **2** or **3** with excess *m*-CPBA gave the bissulfones **4** or **5** in smooth reactions and 66 or 71% yield (Scheme 1). However, the thermal elimination of phenylsulfinic acid from **2** did not give more than 5% of the desired 9-oxabicyclo[3.3.1]nona-2,6-diene.

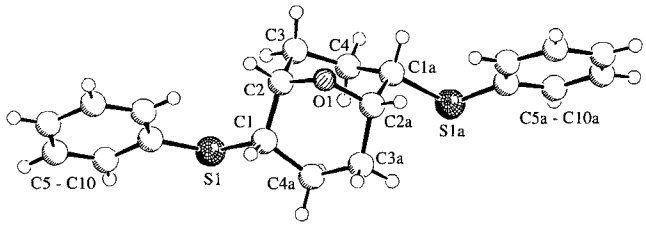


Fig. 1 SCHAKAL plot of compound **2**

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Experimental

Melting points: Heiztischmikroskop Koffler, Reichert, Austria (uncorrected). – column chromatography: silica gel 60 (70–230 mesh), Merck. – ^1H and ^{13}C NMR spectra: Bruker WM 300, ($CDCl_3$, TMS as internal standard). – IR spectra: Nicolet 5DXC-FT-IR. – GLC: HP5890 Series II, Hewlett-Packard, FID, HP-5 capillary, N_2, pressure 0.5 bar. – mass spectra (70 eV): Varian GC 3400/Varian Saturn II (Ion Trap) and Finnigan MAT 8230/SS 300. – Elemental analyses: Analytisches Laboratorium des Organisch-Chemischen Instituts, Universität Münster. – X-ray crystal structure analysis: Enraf Nonius CAD-4 diffractometer, data reduction MolEN, structure solution SHELXS-86 [12], structure refinement SHELXL-93 [13], graphics SCHAKAL-92 [14].

Synthesis of the Bis(phenylsulfenyl) Substituted 9-Oxabicyclononanes 2 and 3

A 500 mL three-necked flask equipped with reflux condenser, thermometer, addition funnel and a magnetic stirrer is charged with a solution of 7.5 mL (6.50 g, 60 mmol) cycloocta-1,5-diene, sulfuric acid (3 mL) and 125 mL of the respective solvent. In the case of methanol dry solvent is used. Phenylsulfenyl chloride (22.5 g, 156 mmol) is added dropwise

over 5–10 min while the solution is stirred vigorously. The reaction mixture is stirred and refluxed for additional 24 h when 250 mL of water are added. The solution is extracted three times with each 250 mL of cyclohexane. Combined organic extracts are dried over $MgSO_4$ and stripped under vacuum to afford a white solid residue containing the desired compounds and diphenyldisulfide. A filtered sample is used to determine the ratio of **2** and **3** by gas chromatography. Compounds **2** and **3** (10.8 g, 53%) are separated by column chromatography (cyclohexane : ethyl acetate 10:1). Both compounds are obtained as white solid plates.

endo,endo-2,6-Bis(phenylsulfenyl)-9-oxabicyclo[3.3.1]-nonane (**2**)

Yield 2.6 g (13%), *m.p.* 81 °C (cyclohexane:ethyl acetate 10:1). – ^{1}H NMR: δ/ppm = 1.74–2.25 (m, 8H, 3-CH_2, 4-CH_2, 7-CH_2, 8-CH_2), 3.53–3.62 (m, 2H, 2-CH, 6-CH), 3.81 (dm, $^3J_{H,H\,(cis)}$ = 5.1 Hz, 2H, 1-CH, 5-CH), 7.08–7.24 (m, 6H, 13-CH, 13'-CH, 14-CH, 14'-CH, 15-CH, 15'-CH), 7.28–7.36 (m, 4H, 12-CH, 12'-CH, 16-CH, 16'-CH). – ^{13}C NMR: δ/ppm = 24.9 (t, 4-CH_2, 8-CH_2), 27.0 (t, 3-CH_2, 7-CH_2), 47.8 (d, 2-CH, 6-CH), 68.7 (d, 1-CH, 5-CH), 127.0 (d, 14-CH, 14'-CH), 129.2 (d, 13-CH, 13'-CH, 15-CH, 15'-CH), 131.4 (d, 12-CH, 12'-CH, 16-CH, 16'-CH), 134.3 (s, 11-C, 11'-C). – MS (GC-MS, 70 eV) *m/z* (%) = 343 (20) [M^+ + 1], 342 (100) [M^+], 314 (2) [342 – CO], 233 (8) [M^+ – C_6H_5S], 232 (14) [M^+–C_6H_5SH], 206 (12) [232 – C_2H_2], 189 (22) [233 – C_3H_8], 162 (10) [206 – C_3H_8], 136 (42) [162 – C_2H_2], 123 (78) [233 – C_6H_5SH], 109 (26) [123 – CH_2], 97 (64) [123 – C_2H_2], 95 (44) [123 – C_2H_4], 91 (22) [109 – H_2O], 81 (16), 79 (56) [97 – H_2O], 69 (38) [97 – CO], 67 (36) [95 – CO], 65 (24) [81 – C_2H_2], 45 (20), 41 (44) [69 – C_2H_4]. – IR (KBr): ν/cm^{-1} = 3055 (m, ν C-H arom.), 2980 (m, ν C-H_2), 2924 (s, ν C-H_2), 1637 (m, ν C=C), 1617 (m, ν C=C), 1582 (m, ν C=C), 1480 (s, δ C-H), 1092 (m), 1055 (m, ν C–O), 1025 (m), 922 (m, ν C-H), 752 (s), 693 (s, ν C–S).

$C_{20}H_{22}OS_2$ calcd.: C 70.14 H 6.47
(342.51) found: C 69.88 H 6.51.

X–ray Crystal Structure Data of **2** [11]: Formula $C_{20}H_{22}OS_2$; M = 342.50; colorless crystal, 0.30 × 0.20 × 0.10 mm; a = 22.215(2), b = 10.256(1); c = 7.583(1) Å, V = 1727.7(3) Å^3, ρ_{calc} = 1.317 gcm^{-3}, F(000) = 728 e, μ = 27.91 cm^{-1}, empirical absorption correction *via* φ scan data (0.868 ≤ C ≤ 0.999), Z = 4, orthorhombic; Pbcn (No. 60); λ = 1.54178 Å, T = 223 K, $\omega/2\Theta$ scans, 1762 reflections collected (– h + k – l), [(sinΘ)/λ] = 0.62 Å^{-1}, 1762 independent and 1649 observed reflections [I ≥ 2 σ(I)], 152 refined parameters, R = 0.034, wR^2 = 0.097, max. residual electron density 0.22 (–0.14) e Å^{-3}, disorder in the core of the molecule (0.667(4) : 0.333(4), hydrogens calculated and refined as riding atoms.

endo,endo-2,5-Bis(phenylsulfenyl)-9-oxabicyclo[4.2.1]-nonane (**3**)

Yield 4.9 g (24%), *m.p.* 77–79 °C (cyclohexane:ethyl acetate 10:1). – ^{1}H NMR: δ/ppm = 1.76–2.23 (m, 8H, 3-CH_2, 4-CH_2, 7-CH_2, 8-CH_2), 3.50–3.62 (m, 2H, 2-CH, 5-CH), 4.44–4.53 (m, 2H, 1-CH, 6-CH), 7.11–7.23 (m, 6H, 13-CH, 13'-CH, 14-CH, 14'-CH, 15-CH, 15'-CH), 7.28–7.37 (m, 4H, 12-CH, 12'-CH, 16-CH, 16'-CH). – ^{13}C NMR: δ/ppm = 27.0 (t, 7-CH_2, 8-CH_2), 28.7 (t, 3-CH_2, 4-CH_2), 51.9 (d, 2-CH, 5-CH), 80.6 (d, 1-CH, 6-CH), 126.9 (d, 14-CH, 14'-CH), 129.0 (d, 13-CH, 13'-CH, 15-CH, 15'-CH), 131.5 (d, 12-CH, 12'-CH, 16-CH, 16'-CH), 135.2 (s, 11-C, 11'-C). – MS (GC–MS, 70 eV) *m/z* (%) = 343 (22) [M^+ + H], 342 (100) [M^+], 314 (2) [342 - CO], 233 (36) [M^+ – C_6H_5S], 232 (10) [M^+ – C_6H_5SH], 206 (10) [232 – C_2H_2], 189 (16) [233 – C_3H_8], 162 (10) [206 – C_3H_8], 136 (36) [162 – C_2H_2], 123 (70) [233 – C_6H_5SH], 109 (18) [123 – CH_2], 97 (42) [123 – C_2H_2], 95 (35) [123 – C_2H_4], 91 (16) [109 – H_2O], 79 (42) [97 – H_2O], 67 (24) [95 – CO], 55 (15) [$C_4H_7^+$], 41 (32) [67 – C_2H_2].

$C_{20}H_{22}OS_2$ calcd.: C 70.14 H 6.47
(342.51) found: C 70.13 H 6.63.

Tab. 2 Selected bond lengths (Å) and bond angles (°) of compound **2** [11]

S(1)–C(5)	1.745(3)	C(5)–S(1)–C(1)	106.4(2)
S(1)–C(1)	1.861(4)	C(4)1–C(1)–C(2)	112.4(2)
C(1)–C(4)#1	1.534(3)	C(4)1–C(1)–S(1)	106.4(2)
C(1)–C(2)	1.536(4)	C(2)–C(1)–S(1)	113.9(2)
C(2)–O(1)	1.434(3)	O(1)–C(2)–C(3)	109.4(2)
C(2)–C(3)	1.521(4)	O(1)–C(2)–C(1)	108.7(2)
C(3)–C(4)	1.517(5)	C(3)–C(2)–C(1)	117.8(2)
C(4)–C(1)#1	1.534(3)	C(4)–C(3)–C(2)	113.8(2)
S(1A)–C(1A)	1.748(10)	C(3)–C(4)–C(1)#1	111.1(3)
S(1A)–C(5)	1.795(8)	C(1A)–S(1A)–C(5)	106.9(4)
C(1A)–C(2A)	1.524(8)	C(2A)–C(1A)–C(3A)	113.1(4)
C(1A)–C(3A)	1.537(7)	C(2A) –C(1A)–S(1A)	111.3(4)
C(2A)–O(1)	1.449(6)	C(3A)–C(1A)–S(1A)	108.6(5)
C(2A)–C(4A)#1	1.537(8)	O(1)–C(2A)–C(1A)	109.2(4)
C(3A)–C(4A)	1.498(11)	O(1)–C(2A)–C(4A)#1	108.3(4)
C(4A)–C(2A)#1	1.537(8)	C(1A)–C(2A)–C(4A)#1	117.3(5)
C(5)–C(6)	1.391(2)	C(4A)–C(3A)–C(1A)	111.1(6)
C(5)–C(10)	1.391(2)	C(3A)–C(4A)–C(2A)#1	114.1(5)
C(6)–C(7)	1.379(3)	C(6)–C(5)–C(10)	118.8(2)
C(7)–C(8)	1.384(3)	C(6)–C(5)–S(1)	114.8(2)
C(8)–C(9)	1.377(3)	C(10)–C(5)–S(1)	126.3(2)
C(9)–C(10)	1.382(2)	C(6)–C(5)–S(1A)	118.5(3)
O(1)–C(2)#1	1.434(3)	C(10)–C(5)–S(1A)	122.7(3)
O(1)–C(2A)#1	1.449(6)	C(7)–C(6)–C(5)	120.4(2)
		C(6)–C(7)–C(8)	120.6(2)
		C(9)–C(8)–C(7)	119.2(2)
		C(8)–C(9)–C(10)	120.8(2)
		C(9)–C(10)–C(5)	120.2(2)
		C(2)–O(1)–C(2)#1	111.8(2)
		C(2A)–O(1)–C(2A)#1	111.6(4)

Symmetry transformations used to generate equivalent atoms: #1 – x+1,y,–z–1/2

Formation of the Bissulfones 4 and 5

3.5 g (14.2 mmol) *meta*-chloroperbenzoic acid (*m*-CPBA, ca. 70%) are given over 10 min to an ice cold stirred solution of 1.0 g (2.9 mmol) bis(phenylsulfenyl)-9-oxabicyclononane **2** or **3**, respectively in 50 mL of methylene chloride. After stirring for additional 60 min at this temperature the mixture is left stirring to come to room temperature over night. The reaction mixture is extracted with 30 mL of 2N NaOH and then twice with 20 mL of 2N NaOH and finally with 20 mL of water. After drying with $MgSO_4$ the solvent is evaporated *in vacuo*. The products **4** or **5**, respectively, are isolated as white powders.

endo,endo-2,6-Bis(phenylsulfonyl)-9-oxabicyclo[3.3.1]-nonane (**4**)

Yield 1.1 g (66%), *m.p.* 218 °C (ethyl acetate). – ^{1}H NMR: δ/ppm = 1.65–2.03 (m, 4H, 4-CH_2, 8-CH_2), 2.39–2.62 (m, 2H, 3-CH_2, 7-CH_2), 3.48–3.60 (m, 2H, 1-CH, 5-CH), 4.55 (dm, $^3J_{H,H\,(cis)}$ = 5.2 Hz, 2H, 2-CH, 6-CH), 7.54–7.62 (m, 4H, 13-CH, 13'-CH, 15-CH, 15'-CH), 7.64–7.71 (m, 2H, 14-CH, 14'-CH), 7.83–7.91 (m, 4H, 12-CH, 12'-CH, 16-CH, 16'-CH). – ^{13}C NMR: δ/ppm = 20.1 (t, 3-CH_2, 7-CH_2), 25.6 (t, 4-CH_2, 8-CH_2), 62.7 (d, 1-CH, 6-CH), 64.9 (d, 2-CH, 5-CH), 128.5 (d, 12-CH, 12'-CH, 16-CH, 16'-CH), 129.3 (d, 13-CH, 13'-CH, 15-CH, 15'-CH), 134.0 (d, 14-CH, 14'-CH), 138.0 (s, 11-C, 11'-C).

$C_{20}H_{22}O_5S_2$	calcd.:	C 59.09	H 5.45
(406.51)	found:	C 58.94	H 5.42.

endo,endo-2,5-Bis(phenylsulfonyl)-9-oxabicyclo[4.2.1]-nonane (**5**)

Yield 1.2 g (71%), – ^{1}H NMR: δ/ppm = 1.50–2.62 (m, 8H, 3-CH_2, 4-CH_2, 7-CH_2, 8-CH_2), 3.43–3.58 (m, 2H, 1-CH, 6-CH), 4.77 (ddm, $^3J_{H,H\,(trans)}$ = 7.9 Hz, $^3J_{H,H\,(cis)}$ = 4.3 Hz, 2H, 2-CH, 5-CH), 7.56–7.70 (m, 6H, 13-CH, 13'-CH, 14-CH, 14'-CH, 15-CH, 15'-CH), 7.85–7.93 (m, 4H, 12-CH, 12'-CH, 16-CH, 16'-CH). – ^{13}C NMR: δ/ppm = 21.5 (t, 3-CH_2, 4-CH_2), 27.2 (t, 7-CH_2, 8-CH_2), 64.9 (d, 2-CH, 5-CH), 66.7 (d, 1-CH, 6-CH), 128.5 (d, 12-CH, 12'-CH, 16-CH, 16'-CH), 129.4 (d, 13-CH, 13'-CH, 15-CH, 15'-CH), 133.9 (d, 14-CH, 14'-CH), 138.6 (s, 11-C, 11'-C). – MS (70 eV) *m/z* (%) = 406 (4) [M^+], 279 (18), 265 (70) [$M^+ - C_6H_5SO_2$], 264 (50) [$M^+ - C_6H_5SO_2H$], 206 (40) [265 – C_3H_7O], 149 (82) [206 – C_4H_9], 123 (82) [265 – $C_6H_5SO_2H$], 81 (60) [123 – C_3H_6], 69 (72) [123 – C_2H_6], 57 (100) [$C_3H_7O^+$]. – IR (KBr): ν/cm^{-1} = 2937 (m, ν C-H_2), 1624 (m, ν C=C), 1618 (m, ν C=C), 1582 (m, ν C=C), 1448 (m, δ C-H), 1306 (s, ν SO_2), 1300 (s), 1144 (s, ν SO_2), 1085 (w, ν C–O), 728 (w, δ C-H), 689 (w, δ C-H), 609 (s).

$C_{20}H_{22}O_5S_2$	calcd.:	C 59.09	H 5.45
(406.51)	found:	C 58.83	H 5.43.

References

[1] a) J. Beger, J. Prakt. Chem. **1991**, *333*, 677; b) K. E. Harding, T. H. Tiner, Electrophilic Heteroatom Cyclizations in: Comprehensive Organic Chemistry, B. M. Trost, I. Fleming, M. F. Semmelhack, Eds., Vol 4, Pergamon Press, Oxford 1991, pp 363–421

[2] R. M. Scarborough, Jr., A. B. Smith III, W. E. Barnette, K. C. Nicolaou, J. Org. Chem. **1979**, *44* , 1742

[3] K. C. Nicolaou, D. A. Claremon, W. E. Barnette, S. P. Seitz, J. Am. Chem. Soc. **1979**, *101*, 3704

[4] S. Uemura, A. Toshimitsu, T. Aoai, M. Okano, Tetrahedron Lett. **1980**, *21*, 1533

[5] a) S. Uemura, A. Toshimitsu, T. Aoai, M. Okano, J. Chem. Soc., Chem. Commun. **1979**, 610; b) A. Toshimitsu, T. Aoai, S. Uemura, M. Okano, J. Org. Chem. **1981**, *46*, 3021; c) A. Toshimitsu, T. Aoai, H. Owada, S. Uemura, M. Okano, Tetrahedron **1985**, *41*, 5301

[6] a) H. Stetter, H. J. Meissner, Tetrahedron Lett. **1966**, 4599; b) H. Stetter, H. J. Meissner, W. D. Last, Chem. Ber. **1968**, *101*, 2889; c) A. C. Cope, M. A. McKervey, N. M. Weinshenker, J. Org. Chem. **1969**, *34*, 2229; d) J. N. Labows, Jr., D. J. Swern, J. Org. Chem. **1972**, *37*, 3004; e) N. V. Averina, N. S. Zefirov, P. P. Kadzjauskas, S. V. Rogozina, N. K. Sadovaja, N. M. Soldatov, Zh. Org. Khim. **1974**, *10*, 1442; J. Org. Chem. USSR, Engl. Trans. **1974**, *10*, 1453; f) G. Haufe, E. Kleinpeter, M. Mühlstädt, J. Graefe, Monatsh. Chem. **1978**, *109*, 575; g) G. Haufe, G. Alvernhe, A. Laurent, J. Fluorine Chem. **1990**, *46*, 83; h) G. Haufe, G. Alvernhe, D. Anker, A. Laurent, C. Saluzzo, J. Org. Chem. **1992**, *57*, 714

[7] G. Haufe, Tetrahedron Lett. **1984**, *25*, 4365

[8] G. A. Jones, C. J. M. Stirling, N. G. Bromby, J. Chem. Soc., Perkin Trans. 2 **1983**, 385

[9] F. G. Bordwell, M. L. Douglass, J. Am. Chem. Soc. **1966**, *88*, 993

[10] The X-ray structure of *endo,endo*-2,5-bis(phenylsulfenyl)-9-oxabicyclo[4.2.1]nonane (**3**) has been published earlier: K. Hegemann, G. Haufe, R. Fröhlich, F. Zippel, Acta Cryst. **1997**, *C53*, 1889

[11] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101437. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk)

[12] G. M. Sheldrick, Acta Cryst. **1990**, *A46*, 467

[13] G. M. Sheldrick, SHELEXL-93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany, 1993

[14] E. Keller, SCHAKAL-92. Program for the graphic representation of molecular and crystallographic models, University of Freiburg, Germany, 1992

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