127. Reactions of Sulfinylated Radicals. Stereoselectivity in Six-Membered Rings

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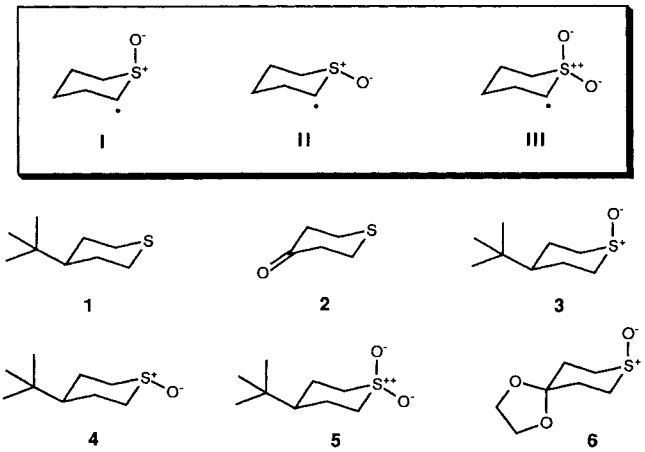
The allylation and deuteration of six-membered cyclic sulfinylated radicals were investigated. For this purpose, radicals with the predefined conformations **I** and **II** were generated from 2-(phenylselenenyl)thiacyclohexane-1-oxide derivatives **7–10** (*Scheme*). Steric effects were insufficient to account for all the observed selectivities. The participation of stereoelectronic effects are envisaged to explain the stereoselective axial deuteration of type-**II** radicals.

Introduction. – Sulfoxides have been widely used for the synthesis of enantiomerically pure compounds (EPC synthesis [1]) [2]. Different types of key reactions, based mainly on nucleophilic reagents [3] (α-deprotonated sulfoxides), electrophilic reagents [4] (α,β-unsaturated sulfoxides), rearrangements [5], and the *Pummerer* reaction [6], have been employed. The use of sulfoxides as chiral auxiliary for radical reactions is of great interest. Highly stereoselective reactions are expected from radicals adjacent to the chiral S-center. We have already reported that no racemization of the stereogenic center occurs during the radical reduction of optically pure (*R*)-chloromethyl tolyl sufoxide to (*S*)-methyl tolyl sulfoxide [7]. Our initial attempt to control the stereoselectivity of radical cyclization with a sulfinyl group failed [7][1])[2]). In order to understand the effect of a



[1]) *Tsai et al.* have reported very similar cyclizations with low stereoselectivities induced by the S-center [8].

[2]) During the preparation of this manuscript, a highly stereoselective cyclization of a radical generated by MnIII/CuII oxidation of a β-ketosulfoxide was reported by *Snider et al.* [9].

sulfinyl group next to the radical center on the stereochemical outcome of the reaction, we decided to begin a systematic study with rigid six-membered ring systems[3]) of known conformation. The stereoselectivity in six-membered cyclic radicals is usually governed by three effects [11]: tortional, steric, and stereoelectronic effects. Tortional effects, which were introduced by analogy with the case of cyclohexanone reduction [12], always favored the axial attack at the radical center. Steric effects are of two types: 1,2-interactions for both axial and equatorial substituents favoring the '*anti*' mode of approach and 1,3-diaxial interactions disfavoring the axial attack at the radical center. The existence of stereoelectronic effects is only well documented for anomeric glycosyl radicals [13]. We report here our investigations of radicals derived from thiacyclohexane 1-oxide with the O-atom in axial (**I**) and equatorial (**II**) positions. The inherent effect to the cycle was examined on the radical derived from thiacyclohexane 1,1-dioxide (**III**).

Results and Discussion. – *Preparation of the Radical Precursors.* For the generation of the radicals, the selenenylated derivatives **7**–**9** and sulfone **10** were prepared. Sulfide **1** was oxidized according to [14] with *tert*-butyl hyprochlorite to give the axial sulfoxide **3**[4]). Inversion of sulfoxide **3** *via* the ethoxysulfonium salt [15] gave diastereoisomerically pure **4**. Sulfone **5** was prepared by 3-chloroperbenzoic-acid oxidation of **1**. The sulfoxide **6** was obtained from thiacyclohexan-4-one (**2**) by oxidation with sodium periodate and acetalization with ethylene glycol. The selenenylated compounds **7**–**10** were prepared from **3** to **6** in 60–75% yield using 2 equiv. of lithium diisopropylamide (LDA) and 1 equiv. of diphenyl diselenide[5]) in THF according to the procedure reported for the selenenylation of nitriles [16].

Radical Reactions. Two different reactions, the deuteration with tributyltin deuteride and the allylation with allyltributylstannane[6]), were investigated. The radical of type **I** generated from **7** was allylated at 80° to give **11a**/**11b** (1:2.3) and deuterated with formation of **12a**/**12b** (1:1.2; *Scheme*). The preferential attack '*syn*' to the S–O bond with formation of the equatorially substituted products **11b** and **12b** indicates that the reaction is mainly controlled by 1,3-diaxial interactions. The orientation of the semi-occupied orbital makes such interactions particularly important (see radical **A** in *Fig. 1*). The higher selectivity observed for the allylation results from the larger size of the allylating reagent relative to tributyltin deuteride which enhances 1,3-diaxial interactions. In the same way, allylation and deuteration of radical **B**[7]), generated from **8**, also occurred preferentially '*syn*' to the S–O bond giving **13a**/**13b** (1:9) and **14a**/**14b** (1:2.3), respectively. The high equatorial selectivity observed in that particular case is caused by the presence of an axial O-atom in 4-position which reinforces 1,3-diaxial interactions.

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[3]) *Waldner et al.* have very recently reported a study of a five-membered sulfinylated cyclic radical issued from a cyclic sulfinamide [10].

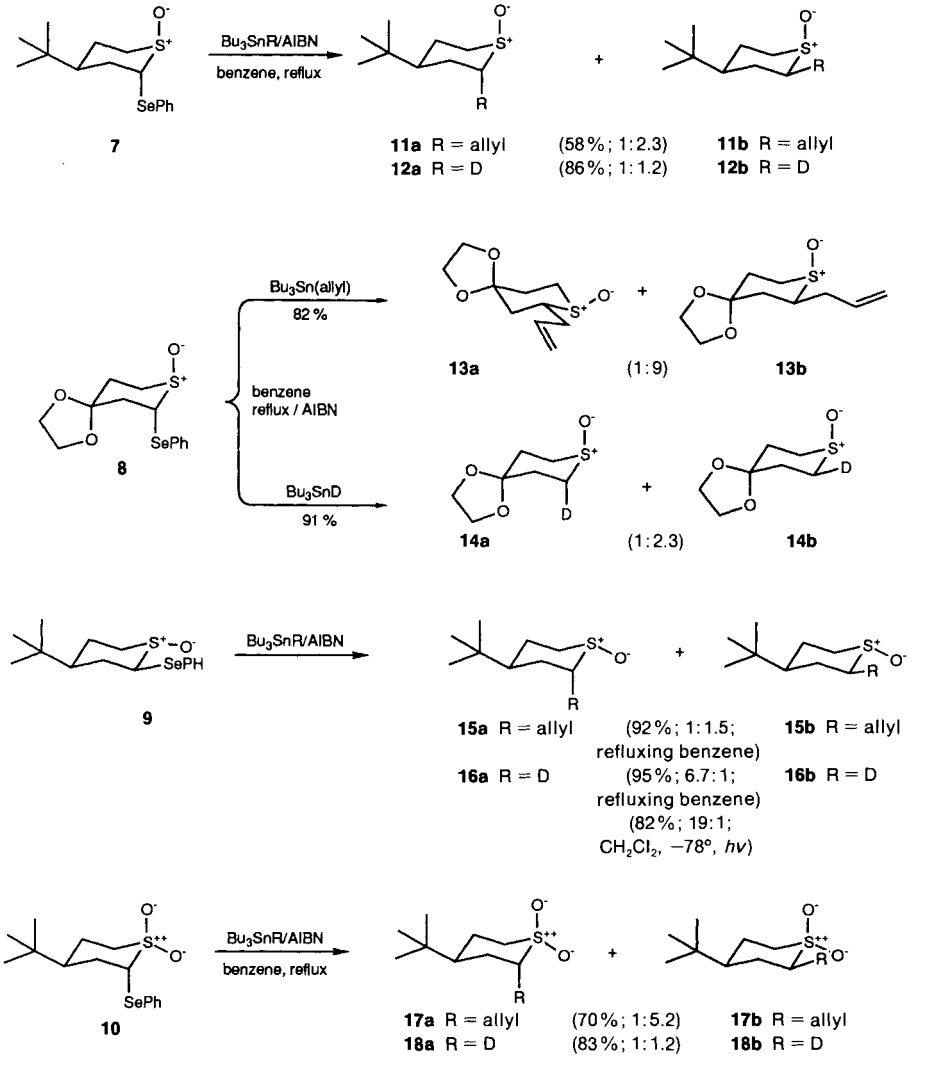
[4]) This reaction is not completely stereoselective as reported in the literature, a 8:1 mixture of isomers **3**/**4** was formed. No purification was possible at this stage.

[5]) The use of benzeneselenenyl chloride led to a mixture of mono- and diselenenylated products.

[6]) Most of the reactions reported here were performed in benzene for practical reasons. Only very slight differences of stereoselectivity were observed when the reactions were run in CH_2Cl_2 indicating that the sulfoxide complexation by benzene [17] is insignificant.

[7]) We assume that the preferred conformation of radical **B** is the same as the conformation of the unsubstituted sulfoxide **6**. The axial position of the O-atom was deduced from NMR spectra according to [18].

Scheme



A radical of type **II** was examined next. Both 1,3- and 1,2-steric interactions should favor an attack at the radical center '*anti*' to the S–O bond with formation of the equatorial derivative. The allylation of **9** *via* radical **C** occurred with an unexpected very low preference for the equatorial isomer to give **15a**/**15b** as a 1:1.5 mixture of isomers. The selectivity is even reversed for the radical deuteration of **9** which gave preferentially the axial isomer **16a** arising from a '*syn*' attack relative to the S–O bond: product ratios **16a**/**16b** of 6.7:1 and 19:1 were observed for the reaction in refluxing benzene and in CH_2Cl_2/Et_2O under irradiation at −78°, respectively. Steric effects do not account for the observed stereoselectivities. Only a stereoelectronic effect orienting the attack at the radical center '*anti*' to the lone pair of the S-atom which permit a good overlap between

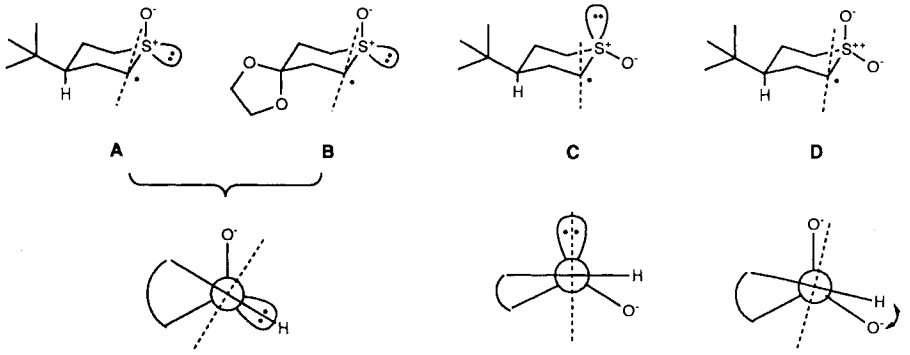


Fig. 1. *Conformation of radicals* **A**–**D**. The dashed line shows the orientation of the singly occupied orbital.

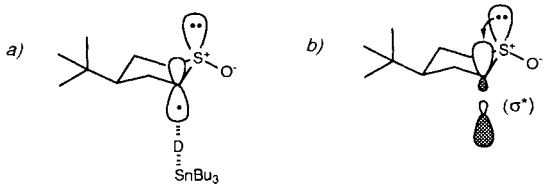


Fig. 2. *Transition state stabilized by stereoelectronic effects for the deuteration of radical* **C**. See text.

this lone pair and the bond being formed may explain this result (*Fig. 2a*). Possible pyramidalization of the radical center in the transition state [19] may favorise the orbital overlap (true diaxial arrangement). The energy of the transition state is lowered by the delocalization of the nonbonded electron pair of the S-atom into the antibonding component of the bond in formation[8]) (*Fig. 2b*; *vide infra*). A colinear arrangement of the S lone pair and the semi-occupied orbital leads to a decrease of 1,3-diaxial steric interactions compared to type-**I** radicals (*Fig. 1*).

In order to test the orienting effect of the axial nonbonding electron pair at the S-atom, we looked at the sulfonylated radical **D** (type **III**). This radical differs from **C** only be the replacement of the axial nonbonding pair of electrons at the S-atom by a S–O bond. A dramatic change of stereoselectivity was observed. The allylation of **10** gave **17a**/**17b** in a ration of 1: 5.2, a result fully explained by 1,2- and 1,3-steric effects. The high selectivity for the axial isomer observed for the deuteration of **9** was also lost when the reaction was performed with **10**, in which a 1:1.2 mixture of **18a**/**18b** was isolated. The slight preference for the formation of the equatorial isomer is very similar to the deuteration of sulfoxide **7**. The repulsive interaction between the equatorial S–O bond and the C–H bond of the radical center which reorientates slightly the semi-occupied orbital (see *Fig. 1*, *Newman* projection) has no observable effect. *E.g.*, the 1,3-diaxial interactions are

[8]) A stereoelectronic control of face selection in the capture of substituted adamantyl radicals was reported [20]. The stereoselectivity was ascribed to transition-state hyperconjugation, a hypothesis similar to the one we present here.

not significantly weakened relative to radical **A** or **B**. These results support our hypothesis about a stereoelectronic control of reactions of type-**II** radical.

Conclusion. – The comprehension of the factors governing the stereoselectivity of cyclic sulfinylated radicals is of importance for further development of synthetic methods based on sulfinylated radicals. We have demonstrated that not only steric effects play a role in the stereochemical outcome of the reactions but also stereoelectronic effects. For a sulfinyl group adjacent to the radical center, 1,2-steric effects and stereoelectronic effects are opposite. The former induces attack at the radical center '*anti*' to the S–O bond and the latter favors the '*anti*' approach relative to the nonbonding electron pair at the S-atom ('*syn*' relative to the S–O bond). Stereoelectronic effects are particularly important for small reagents like tributyltin deuteride. The reactions with larger substrates like olefins are mainly governed by the steric contribution. More information about the structure of cyclic sulfinylated radicals[9]) would be of much interest for a greater comprehension of the problem.

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Experimental Part

General. THF was freshly distilled from K under N_2. CH_2Cl_2 was distilled from P_2O_5. Benzene was distilled from CaH_2 under N_2. Allyltributyltin was filtrated through silica gel (petroleum ether) just prior to use [23]. LDA (1M) was prepared by treating at −78° a soln. of $(i\text{-}Pr)_2NH$ (15 ml, 105 mmol; distilled from CaH_2) in THF (22.5 ml) with 1.6M BuLi (62.5 ml, 100 mmol, in hexane) and stored in a brown bottle in a freezer. Sulfide **1** was prepared according to [14] and sulfide **2** was commercially available. Flash column chromatography (FC): *Merck* silica gel *60* (70–230 mesh). TLC: *Merck* silica gel *60* F_{254} anal. plates; detection either with UV, I_2 or by spraying with a soln. of 25 g of phosphomolybdic acid, 10 g of $Ce(SO_4)_2 \cdot 4\ H_2O$, 60 ml of conc. H_2SO_4, and 940 ml of H_2O with subsequent heating (sulfoxides appear as characteristic yellow spots before heating). GC: *Hewlett-Packard 5710A, SE 30*, 3 m (packed column), and *Carlo Erba, DB-1*, 50 m (capillary column). Bulb-to-bulb distillations: *Büchi-GKR-50* apparatus; b.p. refer to air-bath temp. M.p.: not corrected; *Büchi-Tottoli apparatus. IR: Perkin-Elmer-297* spectrophotometer. NMR: *Bruker AC-200 FT* (200 MHz, ^1H, ^2H) and *AC-250 FT* (250 MHz, ^1H, ^{13}C); unless otherwise indicated, $CDCl_3$ solns.; chemical shifts in δ rel. to TMS (= 0 ppm). MS: *Finnigan 1020* and *Nermag R10-10C*.

General Procedure 1: Selenenylation of Sulfoxides. The sulfoxide (10 mmol) in THF (40 ml) was treated at −78° with 1M LDA (20 ml, 20 mmol). After 30 min stirring at −78°, a soln. of diphenyl diselenide (3.12 g, 10 mmol) in THF (10 ml) was added slowly. The flask was taken out of the cooling bath and stirred for 1 h and the mixture poured in 10% aq. NH_4Cl soln. (150 ml) and extracted with Et_2O (3 × 100 ml). The org. layers were washed with sat. NaCl soln., dried ($MgSO_4$), and evaporated. The crude product was purified by FC.

General Procedure 2: Allylation of α-(Phenylselenenyl)sulfoxides. A soln. of the α-(phenylselenenyl)sulfoxide (2.0 mmol), allyltributyltin (830 mg, 2.5 mmol), and 2,2′-dimethyl-2,2′-azobis[propanenitrile] (= 2,2′-azobisisobutyronitrile; AIBN; 20 mg) in benzene (5 ml) was refluxed under N_2. The reaction was followed by TLC, AIBN (20 mg) was added every 5 h to the mixture until complete disappearence of the starting material. The solvent was evaporated and the residue filtrated through silica gel (AcOEt/petroleum ether 1:5, AcOEt/MeOH 20:1) to give the crude product which was analyzed for diastereoselectivity by ^1H-NMR, ^{13}C-NMR, and GC. For anal. purposes, the products were purified by FC or recrystallized.

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[9]) Acyclic sulfinylated radicals have already been studied by ESR spectroscopy [21]. The results are not relevant for our work, since the measurement were made in H_2O, a highly coordinating solvent for sulfoxides [22].

General Procedure 3: Deuteration of α-(Phenylselenenyl)sulfoxides. A soln. of the α-(phenylselenenyl)-sulfoxide (2.0 mmol), tributyltin deuteride (730 mg, 2.5 mmol), and AIBN (20 mg) was refluxed under N_2. The reaction was followed by TLC. After complete disappearence of the starting material, the mixture was treated as in *General Procedure 2*. Diastereoselectivity was determined by ^{2}H-NMR of the crude product.

cis-*4-(*tert-*Butyl)thiane 1-Oxide* (**3**). The preparation from **1** according to [14] gave a 9:1 *cis/trans* mixture of isomers which were not separable neither by recrystallization nor by FC. M.p. 98–99° ([14]: 106–106.5°). ^{1}H-NMR (250 MHz): 0.90 (*s*, *t*-Bu); 1.18 (*tt*, *J* = 12.0, 2.7, H–C(4)); 1.79 (*dm*, *J* = 14.4, H_{eq}–C(3,5)); 2.12 (*qm*, *J* = 14.5, H_{ax}–C(3,5)); 2.42 (*td*, *J* = 14.5, 2.9, H_{ax}–C(2,6)); 3.08 (*dm*, *J* = 14.5, H_{req}–C(2,6)).

trans-*4-(*tert-*Butyl)thiane 1-Oxide* (**4**). Prepared in diastereoisomerically pure form from **3** *via* the ethoxysulfonium salt according to [14]. M.p. 58–60° ([14]: 57–59°). ^{1}H-NMR (250 MHz): 0.88 (*s*, *t*-Bu); 1.20 (*tt*, *J* = 12.0, 3.0, H–C(4)); 1.45 (*qm*, *J* = 13, H_{ax}–C(3,5)); 2.09 (*dm*, *J* = 13, H_{eq}–C(3,5)); 2.59 (*ddd*, *J* = 14.0, 13.0, 3.0, H_{ax}–C(2,6)); 3.41 (*dm*, *J* = 14.0, H_{eq}–C(2,6)).

trans-*4-(*tert-*Butyl)thiane 1,1-Dioxide* (**5**). A soln. of **1** (490 mg, 3.10 mmol) in CH_2Cl_2 (20 ml) was treated with a dried ($MgSO_4$) soln. of 3-chloroperbenzoic acid (3.1 g, 10 mmol) in CH_2Cl_2 (10 ml). After 12 h stirring at r.t., solid KF (3 g) was added, and stirring was continued for 6 h. The solid was filtrated off, and evaporation of the filtrate gave a white solid which was recrystallized from AcOEt/petroleum ether to give pure **5** (540 mg, 92%). M.p. 125–127°. IR (KBr): 2980, 2870, 1410, 1370, 1330, 1290, 1280, 1120, 1110, 860, 715. ^{1}H-NMR (200 MHz): 0.92 (*s*, *t*-Bu); 1.22 (*td*, *J* = 12.0, 2.8, H–C(4)); 1.89 (*qm*, *J* = 13, H_{ax}–C(3,5)); 2.16 (*dm*, *J* = 14, H_{eq}–C(3,5)); 2.93 (*td*, *J* = 14,0, 3.5, H_{ax}–C(2,6)); 3.08 (*dm*, *J* = 14, H_{eq}–C(2,6)). ^{13}C-NMR (62 MHz): 25.37 (*t*); 27.55 (*q*); 32.62 (*s*); 46.33 (*d*); 51.66 (*t*). MS: 190 (0.1, M^+), 175 (8), 134 (100), 117 (10), 109 (30), 106 (14), 95 (1), 83 (1), 79 (3), 69 (23), 67 (25), 57 (92), 41 (81), 39 (23). Anal. calc. for $C_9H_{18}SO_2$ (190.30): C 56.80, H 9.53, S 16.85; found: C 56.63, H 9.26, S 16.79.

1,4-Dioxa-8-thiaspiro[4.5]decane 8-Oxide (**6**). $NaIO_4$ (15.4 g, 72 mmol) was added to a soln. of thian-4-one (**2**; 8.0 g, 69 mmol) in MeOH/H_2O (150 ml/10 ml). The mixture was stirred at r.t. for 6 h, after which Et_2O (100 ml) was added to the mixture and the solid filtrated off. The filtrate was evaporated, the residue dissolved in CH_2Cl_2, and the org. phase dried ($MgSO_4$) and evaporated: thian-4-one 1-oxide (9.1 g, quant.) as a white solid. A soln. of this crude material (2.6 g, 20 mmol), ethylene glycol (3.0 g, 50 mmol), and TsOH (50 mg) in benzene (60 ml) was heated for 12 h under reflux (*Dean-Stark*). The mixture was poured in Et_2O (100 ml) and washed with sat. Na_2CO_3 soln. The aq. phases were extracted with CH_2Cl_2 and the combined org. phases dried ($MgSO_4$) and evaporated: white solid which was recrystallized from Et_2O/heptanes (3.4 g, 96%). M.p. 94.5–96°. IR (KBr): 3000, 2960, 2930, 2890, 1480, 1420, 1365, 1336, 1270, 1210, 1110, 1060, 1030, 1015, 995, 880. ^{1}H-NMR (250 MHz): 1.78 (*dm*, *J* = 14.0, H_{eq}–C(6,10)); 2.47 (*ddd*, *J* = 14.0, 12.5, 3.5, H_{ax}–C(6,10)); 2.82 (*ddd*, *J* = 14.0, 12.5, 3.5, H_{ax}–C(7.9)); 3.04 (*dm*, *J* = 14.0, H_{eq}–C(7,9)); 3.98 (*m*, 2 H–C(2), 2 H–C(3)). ^{13}C-NMR (62 MHz): 26.10 (*t*); 45.47 (*t*); 64.53 (*t*); 64.73 (*t*); 105.78 (*s*). MS: 176 (3, M^+), 148 (8), 129 (2), 116 (1), 99 (100), 86 (4), 83 (7), 63 (3), 55 (40). Anal. calc. for $C_7H_{12}O_3S$ (176.24): C 47.71, H 6.86, S 18.19; found: C 47.80, H 6.88, S 18.18.

*(1*RS,*2*RS,*4*SR*)-4-(*tert-*Butyl)-2-(phenylselenenyl)thiane 1-Oxide* (**7**). From **3** (700 mg, 4.0 mmol; *cis/trans* 9:1) according to *General Procedure 1*. FC (AcOEt/petroleum ether 1:1) and recrystallization from Et_2O/heptanes gave diastereoisomerically pure **7** (840 mg, 64%). White solid. M.p. 76–78°. IR (KBr): 3055, 2960, 2940, 2860, 2830, 1575, 1470, 1440, 1360, 1245, 1055, 1030, 1005, 900, 740, 690. ^{1}H-NMR (200 MHz): 0.90 (*s*, *t*-Bu); 1.18 (*tt*, *J* = 12.0, 2.2, H–C(4)); 1.73 (*dm*, *J* = 13.5, H_{eq}–C(5)); 1.96–2.18 (*m*, H_{ax}–C(5)); 2.21 (*dm*, *J* = 14.0, H_{eq}–C(3)); 2.63 (*ddd*, *J* = 14.0, 12.0, 3.5, H_{ax}–C(3)); 2.94 (*dq*, *J* = 14.5, 3.0, H_{eq}–C(6)); 3.22 (*ddd*, *J* = 14.5, 12.0, 3.0, H_{ax}–C(6)); 4.20 (*q*, *J* = 3.0, H–C(2)); 7.23–7.38 (*m*, 3 arom. H); 7.55–7.65 (*m*, 2 arom. H). MS: 329 (2, M^+), 235 (1), 183 (5), 173 (80), 157 (30), 141 (5), 130 (5), 117 (11), 99 (17), 77 (52), 67 (23), 57 (100), 51 (46). Anal. calc. for $C_{15}H_{22}OSSe$ (329.36): C 54.70, H 6.73, S 9.74, Se 23.97; found: C 54.73, H 6.67, S 9.70, Se 23.99.

trans-*7-(Phenylselenenyl)-1,4-dioxa-8-thiaspiro[4.5]decane 8-Oxide* (**8**). From **6** (2.9 g, 16 mmol) in THF (40 ml) and hexamethylphosphoric triamide (HMPA, 2 ml). The lithiated sulfoxide was only partially soluble in this solvent system. FC (AcOEt) and recrystallization (AcOEt/heptanes) gave **8** (3.31 g, 61%). White crystalline product. M.p. 132–133°. IR ($CHCl_3$): 3060, 2960, 2920, 1575, 1480, 1435, 1108, 1020. ^{1}H-NMR (200 MHz): 1.75 (*dquint.*, *J* = 14.0, 2.5, H_{eq}–C(10)); 2.19 (*ddd*, *J* = 14.5, 4.2, 2.0, H_{eq}–C(6)); 2.55 (*ddd*, *J* = 13.5, 12.5, 3.0, H_{ax}–C(10)); 2.97 (*dd*, *J* = 14.5, 4.0, H_{ax}–C(6)); 2.98 (*ddd*, *J* = 14.0, 5.0, 3.5, H_{eq}–C(9)); 3.55 (*ddd*, *J* = 14.0, 12.5, 3.2, H_{ax}–C(9)); 4.04 (*m*, 2 H–C(2), 2 H–C(3)); 4.25 (*td*, *J* = 4.0, 2.5, H–C(7)); 7.25–7.40 (*m*, 3 arom. H); 7.58–7.65 (*m*, 2 arom. H). MS: 330 (0.4, $[M - 1]^+$), 183 (1), 157 (3), 148 (48), 99 (100), 77 (7), 55 (23). Anal. calc. for $C_{13}H_{16}O_3SSe$ (331.29): C 47.13, H 4.87, S 9.68, Se 23.83; found: C 47.07, H 4.94, S 9.74, Se 23.69.

*(1RS,2RS,4RS)-4-(*tert*-Butyl)-2-(phenylselenenyl)thiane 1-Oxide* (**9**). From sulfoxide **4** (440 mg, 2.5 mmol) according to *General Procedure 1*. FC (AcOEt/MeOH 20:1) and recrystallization (Et_2O/petroleum ether) gave **9** (540 mg, 66%). M.p. 73–75°. IR (KBr): 3060, 2960, 2900, 2860, 1570, 1475, 1440, 1430, 1420, 1365, 1070, 1050, 1040, 750, 695. ^{1}H-NMR (200 MHz): 0.84 (*s*, *t*-Bu); 1.39 (*m*, H–C(4), H_{ax}–C(3), H_{ax}–C(5)); 2.10 (*dm*, J = 12, H_{eq}–C(5)); 2.46 (*dt*, J = 12.0, 3.0, H_{eq}–C(3)); 2.65 (*td*, J = 12, H_{ax}–C(6)); 3.52 (*ddd*, J = 12, 3, 1.5, H_{eq}–C(6)); 3.75 (*dm*, J = 12, H_{eq}–C(2)); 7.20–7.45 (*m*, 3 arom. H); 7.70–7.90 (*m*, 2 arom. H). MS: 329 (2, M^+), 255 (1), 237 (1), 183 (5), 173 (92), 157 (29), 141 (5), 129 (5), 115 (11), 77 (44), 67 (24), 57 (100), 51 (30). Anal. calc. for $C_{15}H_{22}OSSe$ (329.36): C 54.70, H 6.73, S 9.74, Se 23.97; found: C 54.73, H 6.67, S 9.70, Se 23.99.

cis- *and* trans-*4-(*tert*-Butyl)-2-(phenylselenenyl)thiane 1,1-Dioxide* (**10**). From sulfone **5** (340 mg, 1.8 mmol) according to *General Procedure 1*. FC (AcOEt/petroleum ether 1:3) gave **10** (505 mg, 81%) as a mixture of isomers. TLC (AcOEt/petroleum ether 1:3): *cis*-**10**, R_f 0.42; *trans*-**10**, R_f 0.60.

cis-**10**: IR (KBr): 2980, 1580, 1480, 1440, 1372, 1330, 1300, 1140. ^{1}H-NMR (250 MHz): 0.90 (*s*, *t*-Bu); 1.35 (*tt*, J = 12.0, 2.7, H–C(4)); 1.72–1.97 (*m*, H_{ax}–C(3), H_{ax}–C(5)); 2.07–2.22 (*m*, H_{eq}–C(5)); 2.50 (*dq*, J = 14.0, 3.0, H_{eq}–C(3)); 2.95 (*td*, J = 13.8, 3.8, H_{ax}–C(6)); 3.31 (*dt*, J = 14.0, 3.5, H_{eq}–C(6)); 3.96 (*dd*, J = 13.5, 3.8, H–C(2)); 7.25–7.40 (*m*, 3 arom. H); 7.76–7.85 (*m*, 2 arom. H). MS: 346 (20, $[M + 1]^+$), 225 (6), 183 (6), 158 (37), 125 (10), 107 (8), 91 (9), 83 (29), 77 (15), 69 (90), 57 (100), 55 (36).

trans-**10**: ^{1}H-NMR (250 MHz): 0.90 (*s*, *t*-Bu); 1.36–1.52 (*m*, H–C(4)); 1.91 (*tdd*, J = 13.5, 12.0, 3.0, H_{ax}–C(5)); 2.05–2.21 (*m*, H_{eq}–C(5)); 2.33–2.54 (*m*, H_{ax}–C(3), H_{eq}–C(3)); 2.97 (*dq*, J = 14.0, 2.8, H_{eq}–C(6)); 3.59 (*ddd*, J = 14.0, 13.2, 3.7, H_{ax}–C(6)); 4.34 (*q*, J = 2.8, H–C(2)); 7.25–7.40 (*m*, 3 arom. H); 7.70–7.80 (*m*, 2 arom. H).

cis- and *trans*-**10**. Anal. calc. for $C_{15}H_{22}O_2SSe$ (345.36): C 52.17, H 6.42, S 9.28, Se 22.86; found: C 52.28, H 6.46, S 9.20, Se 22.85.

*(1RS,2RS,4SR)- and (1RS,2SR,4SR)-2-Allyl-4-(*tert*-butyl)thiane 1-Oxide* (**11a** and **11b**, resp.). From **7** (165 mg, 0.5 mmol) according to *General Procedure 2*. Filtration through silica gel gave **11a**/**11b** (1:2.3; 60 mg, 58%).

11a: ^{1}H-NMR (200 MHz): 0.90 (*s*, *t*-Bu); 1.29 (*tt*, J = 12.5, 2.5, H–C(4)); 1.73 (*dm*, J = 13.5, H_{eq}–C(3), H_{eq}–C(5)); 1.96–2.47 (*m*, H_{ax}–C(3), H_{ax}–C(5), CH_2=CHCH_2); 2.55 (*td*, J = 13.5, 3.0, H_{ax}–C(6)); 2.90–3.08 (*m*, H_{eq}–C(6), H_{eq}–C(2)); 5.08–5.20 (*m*, CH_2=CHCH_2); 5.65–5.86 (*m*, CH_2=C*H*CH_2).

11b: ^{1}H-NMR (200 MHz): 0.90 (*s*, *t*-Bu); 1.10–2.60 (*m*, 8 H); 2.95 (*dm*, J = 13, H_{ax}–C(2)); 3.15 (*dt*, J = 14.0, 3.1, H_{eq}–C(6)); 5.08–5.20 (*m*, CH_2=CHCH_2); 5.65–5.86 (*m*, CH_2=C*H*CH_2).

11a/**11b**: IR (KBr): 3080, 2960, 2860, 1635, 1445, 1360, 1055, 1010, 910. MS: 214 (6, M^+), 197 (12), 157 (13), 139 (8), 97 (28), 85 (30), 83 (32), 81 (33), 69 (39), 57 (100), 55 (59). Anal. calc. for $C_{12}H_{22}OS$ (214.37): C 67.24, H 10.34, S 14.96; found: C 67.35, H 10.33, S 15.05.

*(1RS,2RS,4SR)- and (1RS,2SR,4SR)-4-(*tert*-Butyl)(2-^{2}H)thiane 1-Oxide* (**12a** and **12b**, resp.). From **7** (100 mg, 0.30 mmol) according to *General Procedure 3*. Filtration through silica gel gave **12a**/**12b** (1:1.2; 45 mg, 86%). ^{2}H-NMR: **12a**, 2.42; **12b**, 3.08.

trans- *and* cis-*7-Allyl-1,4-dioxa-8-thiaspiro[4.5]decane 8-Oxide* (**13a** and **13b**, resp.). From **8** (115 mg, 0.34 mmol) according to *General Procedure 2*. Filtration through silica gel gave **13a**/**13b** (1:9; 61 mg, 82%) which were separated by FC (AcOEt) for anal. purposes.

13a: R_f 0.40 (AcOEt/MeOH 20:1). IR (KBr): 3080, 3060, 2995, 2980, 2920, 2890, 1640, 1480, 1440, 1345, 1220, 1120, 1030, 930, 920, 850, 698. M.p. 101–103°. ^{1}H-NMR (250 MHz): 1.66 (*dd*, J = 14.5, 12.0, H_{ax}–C(6)); 1.83–2.12 (*m*, 2 H–C(10), H_{eq}–C(6)); 2.38 (*dtm*, J = 14.0, 8.0, 1 H, CH_2=CHCH_2); 2.75 (*m*, 1 H, CH_2=CHCH_2); 2.93–3.08 (*m*, H_{ax}–C(7), H_{ax}–C(9)); 3.24 (*ddd*, J = 12.5, 5.0, 3.5, H_{eq}–C(9)); 3.98 (*m*, 2 H–C(2), 2 H–C(3)); 5.10–5.25 (*m*, CH_2=CHCH_2); 5.68–5.85 (*m*, CH=C*H*CH_2). ^{13}C-NMR (62 MHz): 30.86 (*t*); 33.56 (*t*); 35.33 (*t*); 47.09 (*t*); 59.32 (*d*); 64.62 (*t*); 64.83 (*t*); 106.06 (*s*); 118.88 (*t*); 132.98 (*d*). MS: 167 (1), 149 (2), 139 (2), 113 (9), 99 (100), 95 (4), 86 (5), 67 (6), 55 (28).

13b: R_f 0.51 (AcOEt/MeOH 20:1). Colorless oil. IR (film): 3080, 2930, 2890, 1640, 1440, 1420, 1110, 1050, 975, 920. ^{1}H-NMR (250 MHz): 1.62 (*dt*, J = 13.5, 2.5, H_{eq}–C(6)); 1.68 (*dq*, J = 13.5, 2.5, H_{eq}–C(10)); 2.20 (*dd*, J = 13.5, 12.5, H_{ax}–C(6)); 2.16–2.27 (*m*, 1 H, CH_2=CHCH_2); 2.40 (*td*, J = 13.5, 3.2, H_{ax}–C(10)); 2.44–2.58 (*m*, 1 H, CH_2=CHCH_2); 2.62 (*td*, J = 14.0, 3.5, H_{ax}–C(9)); 2.60–2.73 (*m*, H_{ax}–C(7)); 3.04 (*dt*, 14.0, 3.5, H_{eq}–C(9)); 3.85–4.00 (*m*, 2 H–C(2), 2 H–C(3)); 5.06–5.17 (*m*, CH_2=CHCH_2); 5.67–5.86 (*m*, CH_2=C*H*CH_2). ^{13}C-NMR (62 MHz): 24.39 (*t*); 31.62 (*t*); 35.00 (*t*); 44.03 (*t*); 55.13 (*d*); 64.35 (*t*); 64.56 (*t*); 106.39 (*s*); 118.36 (*t*); 133.29 (*d*). MS (2, M^+), 167 (2), 149 (2), 139 (2), 123 (2), 113 (10), 99 (100), 95 (5), 86 (5), 63 (3), 55 (30). Anal. calc. for $C_{10}H_{16}O_3S$ (216.30): C 55.53, H 7.46, S 14.82; found: C 55.58, H 7.56, S 14.82.

trans- *and* cis-*1,4-Dioxa-8-thia(7-^{2}H)spiro[4.5]decane 8-Oxide* (**14a** and **14b**, resp.). From **8** (140 mg, 0.42 mmol) according to *General Procedure 3*. Filtration through silica gel gave **14a**/**14b** (1:2.3; 68 mg, 91%). ^{2}H-NMR: **14a**, 2.80; **14b**, 3.03.

*(1RS,2SR,4RS)- and (1RS,2RS,4RS)-2-Allyl-4-(*tert*-butyl)thiane 1-Oxide* (**15a** and **15b**, resp.). From **9** (122 mg, 0.36 mmol) according to *General Procedure 2*. Filtration through silica gel gave **15a**/**15b** (1:1.5; 71 mg, 92%). Diastereoisomerically pure **15b** (colorless oil) was isolated by FC (AcOEt). **15b**: IR ($CHCl_3$): 3080, 2966, 2865, 1642, 1478, 1425, 1368, 1031, 1021. ^{1}H-NMR (250 MHz): 0.89 (*s*, *t*-Bu); 1.05–1.23 (*m*, H_{ax}–C(3)); 1.26 (*tt*, *J* = 14.0, 2.5, H–C(4)); 1.38–1.57 (*m*, H_{ax}–C(5)); 2.00–2.16 (*m*, H_{eq}–C(3), H_{eq}–C(5)); 2.37 (*dt*, *J* = 13.8, 8.0, 1 H, CH_2=CHCH_2); 2.52–2.70 (*m*, 2 H–C(6)); 2.83 (*m*, 1 H, CH_2=CHCH_2); 3.44 (*ddd*, *J* = 12.5, 4.5, 2.5, H–C(2)); 5.13–5.25 (*m*, CH_2 = CHCH$_2$); 5.72–5.90 (*m*, CH_2=C*H*CH$_2$). ^{13}C-NMR (62 MHz): 24.53 (*t*); 27.42 (*t*); 29.24 (*t*); 32.50 (*s*); 34.21 (*t*); 46.97 (*d*); 51.53 (*t*); 63.06 (*d*); 118.72 (*t*); 133.31 (*d*). MS: 215 (4, $[M + 1]^+$), 197 (35), 157 (8), 141 (14), 109 (15), 95 (17), 81 (10), 69 (15), 57 (100), 55 (26). Anal. calc. for $C_{12}H_{22}OS$ (214.37): C 67.24, H 10.34, S 14.96; found: C 67.18, H 10.29, S 14.86.

*(1RS,2SR,4RS)- and (1RS,2RS,4RS)-4-(*tert*-Butyl)(2-^{2}H)thiane 1-Oxide* (**16a** and **16b**, resp.). a) *In Refluxing Benzene:* From **9** (100 mg, 0.30 mmol) according to *General Procedure 3*. Filtration through silica gel gave **16a**/**16b** (6.7:1; 50 mg, 95%). b) *In CH_2Cl_2/Et_2O at −78°:* A soln. of **9** (86 mg, 0.26 mmol), tributyltin deuteride (120 mg, 0.40 mmol), and AIBN (10 mg) in CH_2Cl_2/Et_2O 1:1 (10 ml) was placed in a 25-ml quartz flask partially submerged in an i-PrOH/dry-ice-cold bath and irradiated for 1 h with a 300-W sunlamp, placed 5 cm away from the flask. Workup similar to *General Procedure 3* gave **16a**/**16b** (19:1; 58 mg, 82%). ^{2}H-NMR: **16a**, 2.60; **16b**, 3.40.

trans- *and* cis-*2-Allyl-4-(*tert*-butyl)thiane 1,1-Dioxide* (**17a** and **17b**, resp.). From **10** (115 mg, 0.33 mmol) according to *General Procedure 2*. Filtration through silica gel (AcOEt) gave **17a**/**17b** (1:5.2; 53 mg, 70%). Colorless oil. **17b**: IR (film): 3080, 2965, 2880, 1640, 1480, 1440, 1370, 1310, 1290, 1140, 920. ^{1}H-NMR (250 MHz): 0.90 (*s*, *t*-Bu); 1.27 (*tt*, *J* = 12.0, 2.5, H–C(4)); 1.51 (*dt*, *J* = 14.0, 12.0, H_{ax}–C(3)); 1.88 (*m*, H_{ax}–C(5)); 2.05–2.32 (*m*, H_{eq}–C(3), H_{eq}–C(5), 1 H of CH_2=CHCH_2); 2.75–2.91 (*m*, H_{eq}–C(6), 1 H of CH_2=CHCH_2); 2.91 (*td*, *J* = 13.5, 3.5, H_{ax}–C(6)); 3.13 (*dt*, *J* = 14.0, 3.5, H–C(2)); 5.11–5.23 (*m*, CH_2CHCH_2); 5.68–5.86 (*m*, CH_2=C*H*CH$_2$). ^{13}C-NMR (62 MHz): 25.36 (*t*); 27.50 (*q*); 29.65 (*t*), 30.56 (*t*); 32.70 (*s*); 46.71 (*d*); 51.63 (*t*); 60.37 (*d*); 118.88 (*t*); 132.99 (*d*). MS: 231 (4, $[M + 1]^+$), 215 (3), 174 (10), 107 (20), 97 (12), 81 (16), 69 (17), 67 (45), 57 (100), 55 (34). Anal. calc. for $C_{12}H_{22}O_2S$ (230.37): C 62.57, H 9.63, S 13.92; found: C 62.42, H 9.70, S 14.06.

Diastereoisomerically pure **17a** was prepared as follows: A soln. of **11a** (30 mg, 0.14 mmol) and $NaIO_4$ (100 mg, 0.47 mmol) in MeOH/H_2O 4:1 (5 ml) was heated under reflux for 12 h. The soln. was filtrated and evaporated. The residue was dissolved in CH_2Cl_2, the soln. dried ($MgSO_4$) and evaporated, and the residue submitted to FC (AcOEt/petroleum ether 1:2): diastereoisomerically pure **17a** (30 mg, 93%). Colorless oil. IR ($CHCl_3$): 3020, 2965, 2870, 1730, 1370, 1250, 1120, 1045. ^{1}H-NMR (200 MHz): 0.90 (*s*, *t*-Bu); 1.37 (*tt*, *J* = 12.0, 3.0, H–C(4)); 1.75–2.20 (*m*, 2 H–C(3), 2 H–C(5)); 2.40 (*ddd*, *J* = 13.5, 12.0, 8.5, 1 H, CH_2=CHCH_2); 2.80–3.10 (*m*, 2 H–C(6), H_{eq}–C(2), 1 H of CH_2=CHCH_2); 5.12–5.25 (*m*, CH_2=CHCH$_2$); 5.60–5.80 (*m*, CH_2=C*H*CH$_2$). ^{13}C-NMR (62 MHz): 25.21 (*t*), 27.12 (*t*); 27.43 (*q*); 32.01 (*t*); 32.41 (*s*); 39.12 (*d*); 47.61 (*t*); 58.94 (*d*); 118.81 (*t*); 133.16 (*d*). MS: 230 (2, M^+), 215 (3), 173 (1), 123 (7), 107 (26), 97 (14), 81 (18), 67 (40), 57 (100), 55 (40).

trans- *and* cis-*4-(*tert*-Butyl)(2-^{2}H)thiane 1,1-Dioxide* (**18a** and **18b**, resp.). From **10** (106 mg, 0.30 mmol) according to *General Procedure 3*. Filtration through silica gel gave **18a**/**18b** (1:1.2; 47 mg, 83%). ^{2}H-NMR: **18a**, 2.93; **18b**, 3.08.

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