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Protiodesilylation of 3-trimethylsilyl-2-thiabicyclo[2.2.1]hept-5-enes and Derivatives: a Stereochemical Study.

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Abstract: *endo-* and *exo*-trimethylsilyl-3-phenyl-2-thiabicyclo[2.2.1]hept-5-enes, the *endo*-trimethylsilyl-*exo*-S-oxide and their S,S-dioxide derivatives were protiodesilylated with fluoride ion. Stereoconvergent reactions were found, affording the *endo*-phenyl derivatives. These results can be rationalised with the hypothesis of a common carbanionic intermediate. In contrast, the desilylation of 3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]heptane gave a mixture of *endo-* and *exo*-isomers, thus proving the involvement of the double bond in the control of the reaction stereoselectivity.

Introduction. Silyl thioketones are a class of compounds characterised by a particularly high reactivity of the carbon-sulfur double bond in either nucleophilic or electrophilic additions as well as in cycloaddition reactions. In this way a variety of compounds containing the Si-C-S unit can be synthesised[1]. Subsequent protiodesilylation of these compounds gives products formally arising from thioaldehydes[2]. During the last decade there has been a large growth in the use of fluoride-promoted desilylation as a methodology for the generation under very mild conditions of species endowed with carbanionic reactivity[3]. The nature of the intermediates and the stereochemistry of the process although investigated[2b,2c,2e,2f,4,5,6], is still under discussion. The high affinity of the fluoride ion towards the silicon atom is the driving force of the reaction, giving rise to a pentacoordinated silicon anion. The substitution of this hypervalent silicon by an electrophile can then proceed either via a concerted reaction or via the formation of a free carbanion, depending on the nature of the silicon-bonded groups. In this context, the stereochemical course of the desilylation in rigid cyclic systems could shed light on the mechanism. In this paper we report an investigation on the stereochemical outcome and the nature of the intermediates involved in the fluoride-promoted protiodesilylation of a series of diastereomeric 3-trimethylsilyl-2-thiabicyclo[2.2.1]hept-5-enes. In these compounds the sulfur atom α to silicon can be oxidised to sulfoxide or sulfone, thus changing its electron-withdrawing (carbanionic stabilising) power.

Results and Discussion. In a previous work[2a], we reported that the reaction of trimethylsilyl phenyl thioketone with cyclopentadiene at 0°C, gave only the *endo*-silyl derivative **1a**. The reaction performed at higher temperature (25°C) revealed, at a more accurate ¹H NMR investigation (200 MHz) on the crude, a 8:1 ratio of 3-*endo* **1a** and 3-*exo*-trimethylsilylphenyl-2-thiabicyclo[2.2.1]hept-5-enes **1b** (Scheme 1). The two products were separated by crystallisation and chromatography (see experimental). The oxidation of **1a** and **1b** to the corresponding sulfones **2a** and **2b** was easily performed with oxone (KHSO₅). The oxidation of **1a** with m-chloroperbenzoic acid at -50°C led to the *exo* sulfoxide **3**[2a] (Scheme 1). For this reason we did not
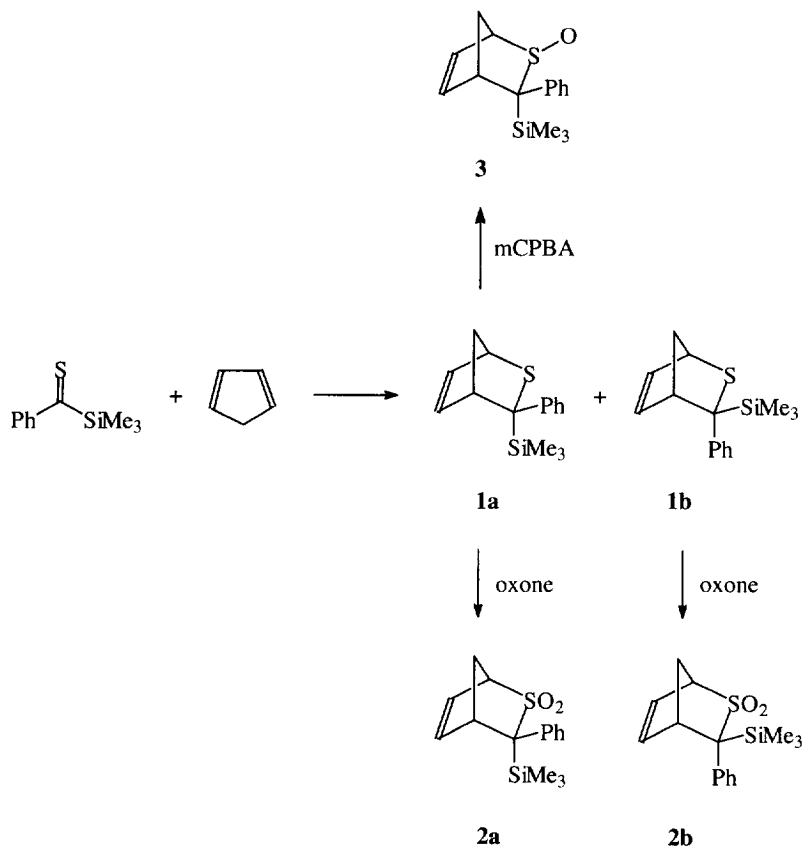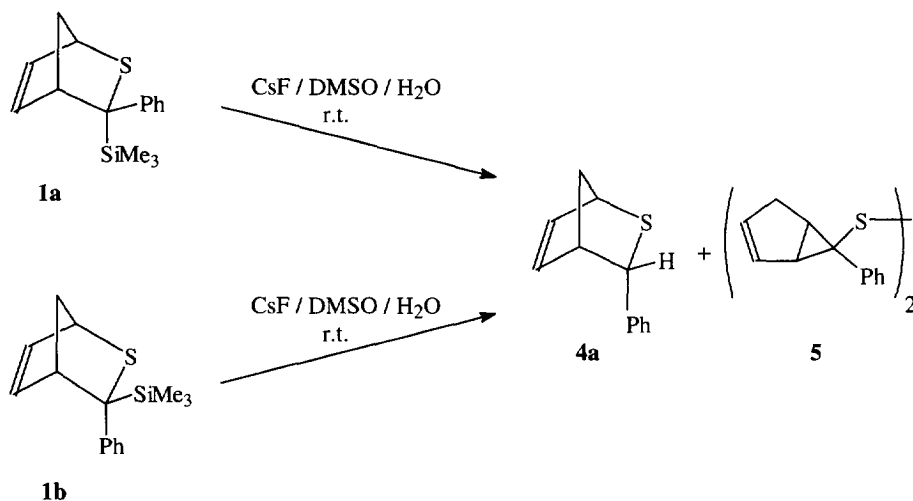
Scheme 1

oxidise the *exo*-silylsulfide **1b**, that would have given a subsequent silyl-Pummerer type rearrangement[7,2d], due to the *syn* coplanar arrangement of the silyl group and the sulphinyl oxygen.

Protiodesilylation of both *endo*-**1a** and *exo*-**1b** sulfides with caesium fluoride in DMSO-water at room temperature afforded stereoselectively the *endo*-phenyl derivative **4a**, besides the disulfide **5** in a 1:1 ratio (from ^{1}H NMR) (Scheme 2).

The reaction was performed in DMSO-d$_6$ and followed by ^{1}H NMR, in order to establish both the exact ratio between products **4a** and **5** and the time needed to complete the desilylation (5 hours for both **1a** and **1b**). Attempted desilylation of **1a** with CsF in acetonitrile as solvent failed; desilylation with tetrabutylammonium fluoride in tetrahydrofuran after 4 days at room temperature gave 80% of the starting material and about 10% of product **5**. Attribution of the *endo* configuration to the protiodesilylated product **4a** was done by a comparison of its ^{1}H NMR spectrum with that of the same product obtained according to the Vedejs procedure[8]. The structure of the disulfide **5** was determined on the basis of its spectral and analytical data (see experimental). In particular its ^{1}H and ^{13}C NMR spectra point to the formation of a single isomer. The observation that both the diastereoisomers **1a** and **1b** gave the same protiodesilylated derivative and the

Scheme 2

disulfide **5** in the same amount in each reaction, suggests that both products are formed from a common intermediate, which could reasonably be assumed to be the carbanion **6** (Scheme 3). The intermediate **6** could be either protonated preferentially in pseudoequatorial position (Scheme 3 path *a*) or could give the thiolate ion **7** through a 2,3-sigmatropic rearrangement, followed by dimerization (Scheme 3 path *b*). The formation of **5** as a single stereoisomer is in agreement with a concerted rearrangement.
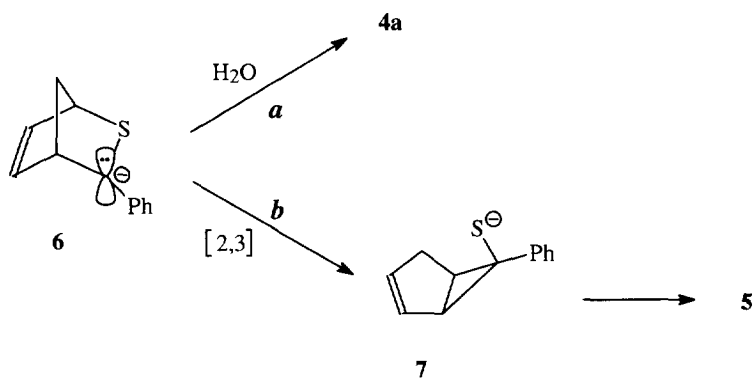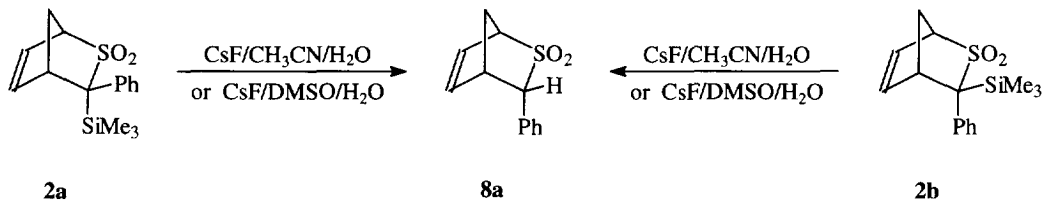

Scheme 3

A similar rearrangement has been reported by Kirby[9] upon treatment of *endo* and *exo*-cycloadducts from ethyl thioxoacetate and cyclopentadiene with LDA and methyl iodide.

Protiodesilylation of *endo*- and *exo*-sulfones **2a** and **2b** with caesium fluoride in DMSO-H_2O at room temperature occurred easily, giving the 3-*endo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene S,S-dioxide **8a** in

almost quantitative yield. Longer times were necessary when performing the desilylation in CH_3CN as a solvent. Also in the case of the sulfones **2a** and **2b** the desilylation was found stereoconvergent (Scheme 4).

Scheme 4

The configuration of **8a** was evinced from n.O.e. experiments. Saturation of the signal of 7-H *syn* to SO_2 at 2.65 ppm, produced a significant increase in the intensity of the 3-H signal at 4.18 ppm. This observation indicates an *exo* position for the 3-H since an *endo* position would put this proton too far apart from 7-H to produce a significant n.O.e., as evaluated from minimised structures. Saturation of the signal at 3.5 ppm (4-H) produced a significant increase in the intensity of the 3-H signal and of the vinylic proton 5-H at 6.58 ppm.

A chemical proof of the configuration of **8a** was obtained by oxidation with oxone of a 3:1 *endo:exo* mixture of 3-phenyl-2-thiabicyclo[2.2.1]hept-5-enes **4a,4b**[10], which gave a mixture of *endo* and *exo*-sulfones **8a** and **8b** in a 3:1 ratio respectively (Scheme 5), as established by ^{1}H NMR.
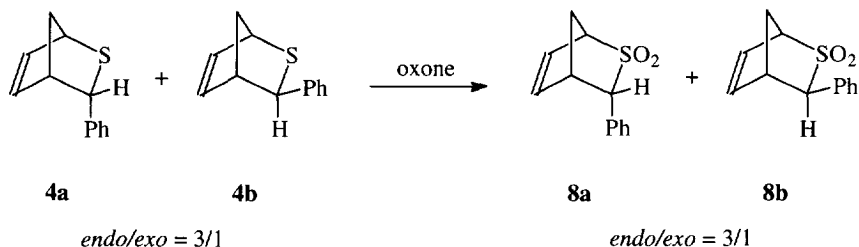
Scheme 5

Protiodesilylation of the 3-*endo*-trimethylsilyl-3-phenyl-2-thiabicyclo[2.2.1]hept-5-ene 2-*exo*-oxide **3** with caesium fluoride in $DMSO-H_2O$ gave exclusively the *endo* phenyl derivative **9** (Scheme 6). Product configuration was again attributed by n.O.e. experiments (see experimental). The observation of stereoconvergent reactions in all the cases examined led to the evidence that all reactions, independently from the oxidation state of the α-sulfur atom, proceed through similar intermediates that are likely to be carbanionic in character, stabilised both by sulfur and phenyl substituents.

The exclusive formation of the *endo* derivatives could simply be explained in terms of an attack of the proton donor from the sterically less hindered *exo*-side. Furthermore, the caesium counterion interacting also

3   9
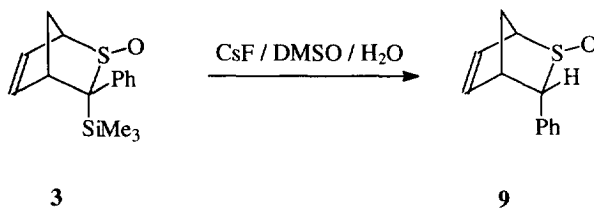
Scheme 6

with the carbon-carbon double bond, can be instrumental in protecting the *endo* side of the carbanion.

The role played by the double bond was evaluated by studying the desilylation of the 3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]heptane **10**. Product **10** was obtained in 48% yield by heterogeneous hydrogenation of **1a** over Ruthenium as a catalyst[11]. Protiodesilylation of the pure isomer **10** was run in the same conditions as for **1a**: in this case the reaction is not stereoselective, affording a mixture of *endo* and *exo* isomers **11a** and **11b** in a 2:1 ratio (Scheme 7).

10   11a   11b
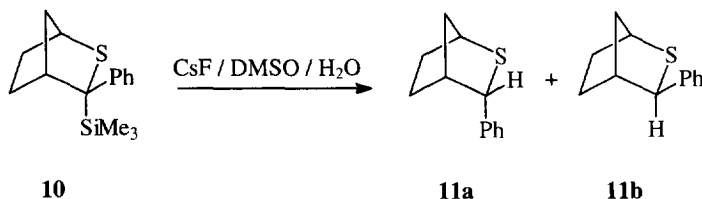
Scheme 7

Attribution of the configuration to the two isomers **11a** and **11b** was based on the well known phenomenon that in these systems the *exo*-3-H resonates at lower field than the *endo*-3-H[12]. In our case the doublet at δ 4.82 was assigned to the pseudo equatorial 3-H of the *endo*-**11a**, while the singlet at δ 4.20 was assigned to the pseudo axial 3-H of the *exo*-**11b**. The result obtained for the desilylation of the saturated derivative **10** confirms the involvement of the double bond in controlling the stereoselectivity of the reaction.

EXPERIMENTAL SECTION

All melting points are uncorrected. I.R. spectra were recorded on a Perkin-Elmer 250 grating spectrometer. NMR spectra were recorded using Varian Gemini 200 or 300 MHz spectrometers and are reported as follows: Chemical Shift [integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, b=broad), coupling constant in Hz, interpretation]. Interpretations were aided in certain cases by decoupling experiments. ^{13}C NMR spectra are reported as follows: chemical shift (multiplicity assigned from DEPT spectra). Mass spectra were recorded at an ionisation potential of 70 eV with a V.G. 7070-E spectrometer. Preparative thick layer chromatography was carried out on glass plates using a 1 mm layer of Merck silica gel 60 PF 254. Diethyl ether was distilled from phosphorus pentoxide and tetrahydrofuran from

sodium. Light petroleum refers to the fraction of b.p. 40-70°C. The composition of the various reaction mixtures is reported as measured by ^{1}H NMR on the crude. In the characterisation of the new compounds elemental analyses have been performed for crystalline products. Oily products, because of the small scale used for the preparation, have been characterised by accurate mass measurements.

3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene 1a and 3-*exo*-trimethylsilyl-3-*endo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene 1b. The cycloaddition was performed on 4.5 mmol scale, as reported previously[2a]: ^{1}H NMR analysis of the crude reaction mixture revealed the presence of the *exo* isomer **1b** in a small amount. The *endo:exo* ratio observed is either 11:1 (cycloaddition run at 0°C) or 8:1 (cycloaddition at 25°C). The two isomers were separated by crystallisation from a small amount of methanol which afforded the main isomer **1a**. Subsequent chromatography of the mother liquor on preparative plates (light petroleum as eluent) afforded the *exo* isomer **1b** as the higher Rf fraction and an additional amount of the *endo* isomer **1a** as the lower Rf fraction. In total 0.89 g of **1a** and **1b** were recovered (76%) when the reaction was run at 25°C. **1b** m.p. 53-54°C (CH_2Cl_2- n-pentane); IR (cm^{-1},CCl_4): 1480, 1440, 1330, 1240; ^{1}H NMR ($CDCl_3$) δ 0.12 (9H, s, $SiMe_3$), 1.62 (1H, dt, J = 10, 7-H), 1.91 (1H, bd, J = 10, 7-H), 3.97 (1H, m, 1-H or 4-H), 4.05 (1H, m, 1-H or 4-H), 5.62 (1H, m, 5-H or 6-H), 6.08 (1H, m, 5-H or 6-H), 7.02-7.56 (5H, m, ArH); ^{13}C NMR ($CDCl_3$) δ 1.3 ($SiMe_3$), 48.8 (7-C), 50.2 and 52.2 (4-C, 1-C), 54.3 (3-C), 124.8, 127.2, 128.2, 134.2, 134.9, 144.4 (5-C, 6-C and ArC); m/z (EI) 260 (M$^+$), 155 (M$^+$-SSiMe$_3$). Anal. Calc. for $C_{15}H_{20}SSi$: C, 69.17; H, 7.74; S, 12.31. Found: C, 69.40; H, 7.48; S, 12.27.

3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene S,S-dioxide 2a. The adduct **1a** (0.18 g, 0.69 mmol) was dissolved in methanol (5 mL) and cooled at 0°C. Then a solution of oxone (KHSO$_5$, 1.23 g, 2 mmol) in water (5 mL) was added. The mixture was stirred for 30 min at 0°C and 2h at room temperature, diluted with water and extracted with chloroform. The organic layer was washed with water, dried and concentrated under reduced pressure giving spectroscopically pure **2a** (0.19 g, 95%) m.p. 165-166°C (MeOH); IR (cm^{-1},CCl_4): 1300, 1130 (SO$_2$), 1250 (SiMe$_3$); ^{1}H NMR ($CDCl_3$) δ 0.1 (9H, s, $SiMe_3$), 2.28 (2H, t, J = 2, 7-H), 3.91 (1H, bs, 4-H), 4.05 (1H, bs, 1-H), 6.37 (1H, q, J = 3, 5-H), 6.69 (1H, dd, ^{1}J = 3, ^{2}J = 0.7, 6-H); ^{13}C NMR ($CDCl_3$) δ 0.5 ($SiMe_3$), 46.9 (7-C), 49.01 (4-C), 67.47 (1-C), 127.26, 128.04, 129.56, 131.5, 137.0, 141.27 (ArC and vinylic-C); m/z (EI) 293 (M$^+$+H), 228 (M$^+$-SO$_2$), 213 (M$^+$-SO$_2$CH$_3$), 155 (M$^+$-SO$_2$SiMe$_3$), 73 (SiMe$_3$). Anal. Calc. for $C_{15}H_{20}O_2SSi$: C, 61.64; H, 6.87; S, 10.95. Found: C, 62.10; H, 6.80; S, 11.05.

3-*exo*-trimethylsilyl-3-*endo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene S,S-dioxide 2b. The product was prepared as for **2a** starting from **1b**; yield 42%, m.p. 143-144°C (MeOH); IR (cm^{-1},CCl_4): 1299, 1129 (SO$_2$), 1246 (SiMe$_3$); ^{1}H NMR ($CDCl_3$) δ 0.12 (9H, s, $SiMe_3$), 2.30 (1H, dm, J = 10, CH$_2$), 2.75 (1H, d, J = 10, CH$_2$), 3.95 (2H, m, 2 CH), 6.10 (1H, m, 5-H or 6-H), 6.60 (1H, m, 5-H or 6-H), 7.15-7.45 (5H, m, ArH); m/z (EI) 213 (M$^+$-SO$_2$CH$_3$), 155 (M$^+$-SO$_2$SiMe$_3$). Anal. Calc. for $C_{15}H_{20}O_2SSi$: C, 61.64; H, 6.87; S, 10.95. Found: C, 62.01; H, 6.85; S, 10.91.

Protiodesilylation of 3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene 1a. One equivalent of solid CsF was added to a solution of **1a** (0.032 g, 0.12 mmol) in DMSO-d$_6$ (0.7 mL) containing

water (2.2 mmol). The mixture was stirred at room temperature and the desilylation was followed by ^{1}H NMR. Desilylation was complete in 5h and the ^{1}H NMR revealed the presence of the two products **4a** and **5** in a 1:1 ratio. The same reaction was performed on a larger scale, starting from 0.4 g (1.5 mmol) of **1a** dissolved in 5 mL of DMSO. After 5h the reaction was quenched with a saturated solution of NH_4Cl and extracted with ether. The ethereal solution was washed three times with water, then dried (Na_2SO_4) and concentrated in vacuo. Chromatography on silica of the crude (9:1 light petroleum: benzene as eluent), afforded product **4a**[8] (0.086 g, 30%) as the higher Rf fraction and product **5** (0.095 g, 33%) as the lower Rf fraction; **5**: oil; IR (cm^{-1},CS_2): 3060, 3020, 2890, 1020, 970, 915, 810, 765, 720, 705, 690; ^{1}H NMR (CDCl$_3$) δ 2.18 (1H, m, CH), 2.49 (1H, m, CH), 2.64 (2H, m, CH$_2$), 5.80 (2H, bs, vinylic-H), 7.12-7.31 (5H, m, ArH); ^{13}C NMR (CDCl$_3$) δ 32.78 and 33.00 (CH), 34.85 (CH$_2$), 41.77 and 42.17 (CH), 44.87 and 44.95 (C), 126.94, 128.38, 129.40, 129.91, 134.58, 145.12 (ArC and vinylic C); MS calcd. for $C_{24}H_{22}S_2$ m/z 374.1158 (M$^+$), found 374.1163; m/z (EI) 374 (M$^+$), 341 (M$^+$-HS), 308 (M$^+$-H$_2$S$_2$), 187 (M$^+$/2), 121 (PhCS).

Desilylation was performed also using CsF in acetonitrile as solvent, but the starting material was recovered quantitatively after three days at room temperature. Desilylation with tetrabutylammonium fluoride in tetrahydrofuran for 4 days at room temperature followed by the usual work up (sat. NH$_4$Cl), gave after preparative TLC, product **5** (10%) besides unreacted **1a** (80%).

Protiodesilylation of 3-*exo*-trimethylsilyl-3-*endo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene 1b. The desilylation was performed both on NMR and preparative scale using the same conditions as described for **1a**. After 5 hours the reaction was complete. The ^{1}H NMR spectrum revealed the presence of products **4a** and **5** in a ratio about 1:1. Chromatography on silica gel plates (9:1 light petroleum: benzene) afforded **4a** (35%) and **5** (32%).

Protiodesilylation of 3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene S,S-dioxide 2a. The desilylation was performed using the same conditions as described for **1a**, starting from **2a** (0.13 g, 0.44 mmol) and CsF (0.1 g, 0.6 mmol) in dimethylsulfoxide (5 mL) and water (0.77 mmol). The reaction was complete after 4 hours and afforded product **8a** in quantitative yield after the usual work up; m.p. 67-69°C (MeOH); IR (cm^{-1},CCl$_4$): 1312, 1213, 1160 (SO$_2$); ^{1}H NMR (CDCl$_3$) δ 2.42 (1H, dm, J = 11.2, 7-H *anti* to SO$_2$), 2.65 (1H, d, J = 11.2, 7-H *syn* to SO$_2$), 3.50 (1H, bs, 4-H), 4.15 (1H, bs, 1-H), 4.18 (1H, d, J = 3.7, 3-H), 6.40 (1H, m, 6-H), 6.58 (1H, m, 5-H), 7.25-7.45 (5H, m, ArH); ^{13}C NMR (CDCl$_3$) δ 44.81 (CH$_2$), 44.0, 63.15, 67.08 (CH), 128.87, 128.99, 130.11, 130.41, 133.1, 138.7 (ArC and vinylic CH); m/z (EI) 156 (M$^+$-SO$_2$), 91 (PhCH$_2$). Anal. Calc. for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49; S, 14.54. Found: C, 65.31; H, 5.40; S, 14.55. The desilylation was also performed with CsF in acetonitrile as solvent. To a solution of **2a** (0.086 g, 30 mmol) in acetonitrile (4 mL) and water (1.54 mmol) an equivalent amount of CsF was added. After 17 hours 0.052 g (80%) of **8a** were obtained.

Protiodesilylation of 3-*exo*-trimethylsilyl-3-*endo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene S,S-dioxide 2b. The desilylation was performed using the same conditions as described for **1a**, starting from **2b** (0.014 g, 0.047 mmol). After 4 hours product **8a** was obtained in quantitative yield. This product was identical (m.p., I.R., ^{1}H NMR) to the product obtained by desilylation of **2a**.

3-*endo*-Phenyl and 3-*exo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene S,S-dioxides 8a and 8b. A solution of oxone (KHSO$_5$, 0.88 g, 1.41 mmol) in H$_2$O (3 mL), was added at 0°C to a solution of a 3:1 *endo:exo* mixture of 3-phenyl-2-thiabicyclo[2.2.1]hept-5-enes **4a** and **4b**[8] (0.09 g, 0.45 mmol) in MeOH (6 mL). The mixture was stirred for 30 min at 0°C and 1h at room temperature, diluted with water and extracted with chloroform. The organic layer was washed with water, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The sulfones were isolated by thick layer chromatography (7:3 light petroleum - ethyl acetate as eluent); the higher Rf fraction was unreacted **4a** and **4b**. The lower Rf fraction was a mixture of the two sulfones **8a** and **8b** (0.031 g, 30%). ^{1}H NMR of this fraction revealed that the two sulfones were formed in the same 3:1 ratio as the corresponding starting sulfides **4a** and **4b**, the major product being the *endo* sulfone **8a**, identical to that obtained by desilylation of **2a** and **2b**. **8b**: ^{1}H NMR (CDCl$_3$) δ 2.50 (1H, dm, 7-H), 2.68 (1H, d, 7-H), 3.62 (1H, bs, 4-H), 3.80 (1H, d, 3-H), 3.95 (1H, bs, 1-H), 6.45 (1H, m, vinylic-H), 6.70 (1H, m, vinylic-H), 7.25-7.45 (5H, m, ArH).

Protiodesilylation of 3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene-2-*exo*-oxide 3. To a solution of **3**[2a] (0.08 g, 0.28 mmol) in dimethylsulphoxide (2 mL) and H$_2$O (1.54 mmol), CsF (0.086 g, 0.32 mmol) was added and the mixture stirred for 2.5h. After the usual work up, ^{1}H NMR of the crude revealed that only 3-*endo*-phenyl-2-thiabicyclo[2.2.1]hept-5-ene-2-*exo*-oxide **9** was formed in 90% yield. The crude was purified by preparative thick layer chromatography (3:7 light petroleum:ethyl acetate as eluent). The lower fraction was product **9** as an oil: IR (cm^{-1},CCl$_4$): 1160 (SO); ^{1}H NMR (CDCl$_3$) δ 2.45 (1H, dt, J = 11.0, 7-H *anti* to oxygen), 2.85 (1H, d, J = 11.0, 7-H *syn* to oxygen), 3.43 (1H, d, 4-H), 3.88 (1H, d, J = 3.0, 3-H), 4.32 (1H, t, 1-H), 6.02 (1H, m, J = 3.0, 5-H), 6.31 (1H, m, 6-H), 7.10-7.60 (5H, m, ArH), ^{13}C NMR (CDCl$_3$) δ 45.62 (CH$_2$), 47.74, 69.20, 78.86 (CH), 127.47, 128.08, 128.87 (2 CH), 138.00, 143.3 (ArC and vinylic-CH); MS Calcd for C$_{12}$H$_{12}$OS m/z 204.0609 (M$^+$), found 204.0615; m/z (EI) 204 (M$^+$), 155 (M$^+$-SOH).

Assignment of configuration was made by n.O.e. experiments: saturation of the 3-H signal at 3.88 ppm, produced a significant increase in the intensity of the 7-H signal *syn* to oxygen at 2.85 ppm and on the 4-H signal at 3.43 ppm. This effect, already observed for the corresponding sulfone, is in agreement with a pseudoequatorial position for 3-H.

3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]heptane 10. A suspension of RuO$_2$ (0.066 g, 0.5 mmol) in 10 mL of MeOH was stirred under H$_2$ pressure (3.5 atm) for 12 hours to activate the catalyst. To this suspension, a solution of **1a** (0.26 g, 1 mmol) in MeOH (10 mL) was added. The reaction was continued for 24 hours at room temperature. The resulting suspension was then filtered through a Celite pad and the filtrate was concentrated in vacuo; ^{1}H NMR revealed that the crude contained a 12:1 mixture of **10** and **1a**. Purification of the crude by preparative thick layer chromatography (light petroleum as eluent) afforded product **10** as fluorescent higher Rf fraction (0.125 g, 48%); m.p. 40-43°C (MeOH). IR (cm^{-1},CCl$_4$): 2960, 1241, 1149, 1140; ^{1}H NMR (CDCl$_3$) δ 0.04 (9H, s, SiMe$_3$), 1.40-2.00 (6H, m, 3 CH$_2$), 3.35 (1H, bd, CH), 3.45 (1H, bs, CH), 7.0-7.55 (5H, m, ArH); ^{13}C NMR (CDCl$_3$) δ 0.20 (SiMe$_3$), 26.82 (CH$_2$), 35.50 (CH$_2$), 42.87 (CH$_2$), 47.16 (CH), 48.96 (CH), 55.04 (C), 125.37 and 127.98 (aromatic CHs), 147.35 (aromatic C); m/z (EI) 262 (M$^+$), 243 (M$^+$-CH$_3$), 189 (M$^+$-SiMe$_3$). Anal. Calc. for C$_{15}$H$_{22}$SSi: C, 68.67; H, 8.46; S, 12.20. Found: C, 67.95; H, 8.39; S, 12.15.

Desilylation of 3-*endo*-trimethylsilyl-3-*exo*-phenyl-2-thiabicyclo[2.2.1]heptane 10. To a solution of 10 (0.09 g, 0.33 mmol) in dimethylsulphoxide (3 mL) and H_2O (2.3 mmol) CsF (0.069 g, 0.45 mmol) was added and the mixture stirred for 2.5h. After the usual work up the crude was purified by preparative thick layer chromatography (20:1 light petroleum:ethyl ether as eluent). The fluorescent oily fraction was a mixture of 11a and 11b in a 2:1 ratio. IR (cm^{-1},CCl_4): 1490, 1447, 1175; ^1H NMR ($CDCl_3$) δ 1.20-2.30 (6H, m, CH_2), 2.70 (1H, bs, 1-H or 4-H, *exo* isomer), 2.80 (1H, bs, 1-H or 4-H, *endo* isomer), 3.45 (1H, bs, 1-H or 4-H, *endo* isomer), 3.55 (1-H, bs, 1-H or 4-H, *exo* isomer), 4.20 (1H, s, 3-H, *exo* isomer), 4.82 (1H, d, J = 2.5, 3-H, *endo* isomer), 7.10-7.70 (10H, m, ArH); ^{13}C NMR ($CDCl_3$) δ 22.58 (CH_2, *endo*), 29.79 (CH_2, *exo*), 35.58 (CH_2, *exo*), 36.00 (CH_2, *endo*), 39.49 (CH_2, *exo*), 45.58 (CH_2, *endo*), 45.91 (CH, *endo*), 46.07 (CH, *exo*), 46.68 (CH, *exo*), 47.40 (CH, *endo*), 55.31 (CH, *endo*), 55.67 (CH, *exo*), 127.04, 126.17, 128.37, 128.52, 128.63, 129.25 (ArC). MS Calcd. for $C_{12}H_{14}S$ m/z 190.0816 (M^+), found 190.0812; m/z (EI) 190 (M^+), 161 (M^+-C_2H_5), 149, 121.

Also in this case the reaction was performed in DMSO-d_6 and followed by ^1H NMR. When the desilylation was completed an *endo:exo* ratio 1.8:1 was calculated by ^1H NMR.

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