STEREOCHEMISTRY OF FLUORIDE-PROMOTED PROTIO-DESILYLATION OF α-THIASILANES

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Abstract- We have investigated the stereochemistry of fluoride-promoted protiodesilylation of α-thiasilanes on a rigid structure like the thiahydrindane, compound in which the stabilization of a negative charge on the carbon α to sulfur can be gradually increased from sulfide to sulfoxide and at last to sulfone. For the desilylation of sulfoxides and sulfones relatively free carbanions can be hypothesized, for sulfides the intermediate can probably be captured, to some extent stereospecifically, by an electrophile.

Introduction

In the last years the organosilicon compounds have received increasing interest.[1] In particular the desilylation of silanes has been largely used in organic syntheses because it represents a simple methodology to generate, under mild conditions, species which can be compared to carbanions for their reactivity towards electrophiles.[2]

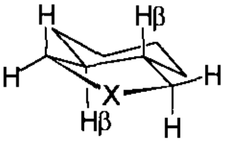
The observed retention of configuration in the desilylative protonation and hydroxyalkylation[2a] of α-silyl sulfides was considered evidence that this reaction proceeds through hypervalent silicon species and not through a free carbanion. In a previous paper[3] we have reported that, in α-silylated sulfones, the reactive species formed by desilylation gave a very unselective distribution of products, independently from the configuration of the starting silyl derivatives. These findings indicate that, in our case, the intermediate is likely to be not a hypervalent silicon species but nearly a free carbanion; in fact, it must be considered that in this latter case a much more stabilized carbanion can be involved. These results are synthetically significant in view of a possible stereochemical control in the formation of new C–C bonds. For this reason we have engaged a study that tries to investigate exclusively the effect exerted by the stabilization of a negative charge on the carbon α to sulfur, stabilization derived from an increased oxidation state of the heteroatom. To that end the protiodesilylation appeared more suitable than a carbodesilylation because in this case any influence of steric hindrance or of electronic effect of the entering electrophile could be excluded.

We have envisaged in the *trans*-2-thiahydrindane a structure in which the stabilization of a negative charge on the carbon adjacent to a sulfurated group can be gradually increased moving from sulfide to sulfoxide and at last to sulfone. The insertion, in these bicyclic compounds, of a trimethylsilyl group α to sulfur would therefore provide a suitable substrate for the study of the stereochemistry of the fluoride-promoted protiodesilylation.

Results and discussion

The conformational rigidity of the *trans*-2-thiahydrindane, the related sulfoxide, and sulfone allows a simple assignment of the quasi-axial and quasi-equatorial hydrogens α to the sulfur atom of these compounds and of the related silyl derivatives in the ^{1}H NMR spectra.

For these compounds (**1**, **2**, and **3**) (Scheme 1) it can be observed that the quasi-axial hydrogens α to the heteroatom are trans-diaxial related to the hydrogens H_β of the bridgehead. By means of the vicinal coupling constant these hydrogens can then be distinguished from the quasi-equatorial ones.



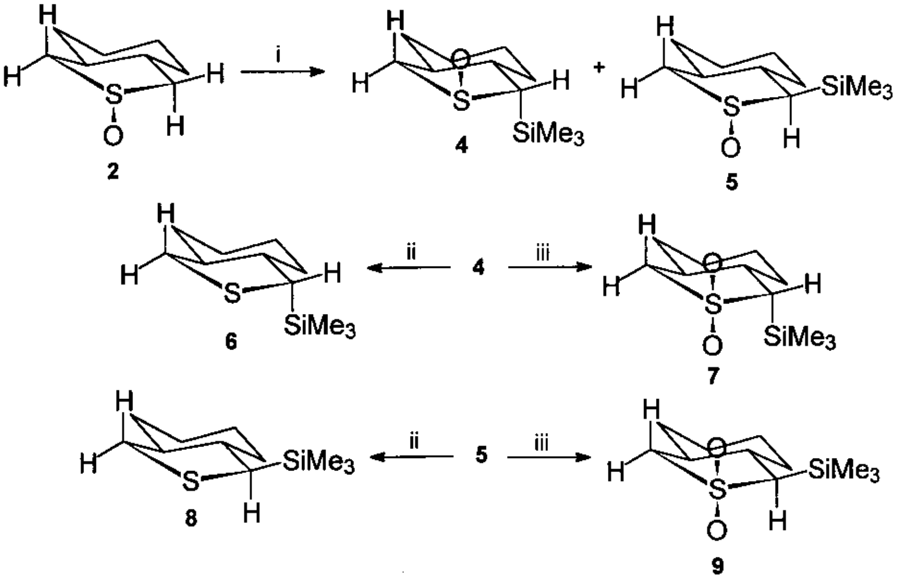
1 X = S; **2** X = SO; **3** X = SO_2

Scheme 1

In particular for the *trans*-thiahydrindane sulfoxide (**2**), it is possible to identify the hydrogens α to SO by means of the chemical shifts and coupling patterns.[4]

All the silylated compounds have been synthesized starting from the *trans*-2-thiahydrindane sulfoxide (**2**) (Scheme 2). Its silylation gave exclusively two isomers (**4**) and (**5**) (separated by flash chromatography), in which, in all likelihood, the silyl group is *trans* to SO. It is in fact reported[5] that the alkylation of sulfoxide of rigid cycles gives *trans* derivatives. Moreover, the *cis*-derivatives would suffer the sila-Pummerer rearrangement. To confirm the configuration of the products, we have made use of the

Europium shift reagents which are known to cause a dramatic differentiation of hydrogens neighbouring a sulfoxide function.[6]



i = LDA, Me_3SiCl; ii = $LiAlH_4$; iii = MCPBA

Scheme 2

In our silylated sulfoxides, three hydrogens α to the SO group are expected: in case of the *trans* isomer two hydrogens are *cis* to the SO while in the *cis* isomer only one hydrogen is *cis* to the sulfoxide. To establish the relationship between SO and $SiMe_3$ groups in the sulfoxides (**4**) and (**5**) we have subjected them to experiments with $Eu(dpm)_3$. In both cases ^1H NMR spectra, obtained in C_6D_6 after addition of increasing amounts of reagent shift, showed considerably greater and comparable downfield shifts for two hydrogens, result consistent with the proposed *trans* configurations.

The sulfoxide (**4**) and (**5**) were reduced with $LiAlH_4$ to give the related sulfides (**6**) and (**8**) or oxidized with MCPBA providing the corresponding sulfones (**7**) and (**9**). The value of the coupling constants related to hydrogens α to sulfide sulfur can exclude any isomerization of $SiMe_3$ group due to $LiAlH_4$. We have also confirmed that the configuration at the $SiMe_3$ group is maintained during the reduction, because the oxidation of the sulfide, derived from reduction of the sulfoxide, to the corresponding sulfone afforded the same compound obtained by direct oxidation of the related sulfoxide to the sulfone.

We applied the synthetic procedure described above to the sulfone because the direct silylation of sulfides is very difficult and besides the two silyl isomers derived from silylation of sulfones can not be separated easily.

A study on silyl derivatives of the *trans*-2-thiahydrindane dioxide was then undertaken to distinguish the isomers with the silyl group axial or equatorial.

For example, the ^1H NMR spectrum of the diastereomer of *trans*-2-thiahydrindane dioxide, obtained from the sulfoxide (**4**), shows a low field doublet, confidently assignable to the proton α to SO_2 and geminal to Me_3Si group. The value of the coupling constant corresponding to the interaction of this hydrogen with the bridgehead hydrogen (J = 7.2 Hz) allows the attribution of a quasi-equatorial conformation of this hydrogen and consequently the silyl group results to be quasi-axial (**7**). The spectrum of the other diastereomer (**9**) can be assigned to the sulfone with the silyl group as quasi-equatorial always observing the value of the coupling constant of the doublet (J = 10 Hz), consistent with axial-axial coupling of the hydrogen geminal to $SiMe_3$ group with the bridgehead hydrogen. Also the chemical shifts of the other two geminal hydrogens α to SO_2 were easily identified by the analysis of coupling constants of the related doublets of doublets (see Experimental Section).

We have unambiguously established the structure of silylated sulfides, *trans* sulfoxides and sulfones with this method, then all these compounds have been subjected to desilylation.

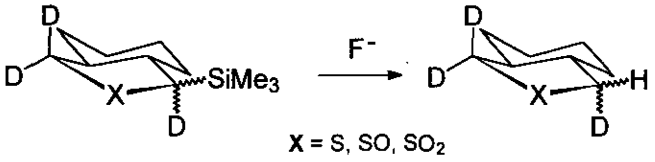
The stereochemistry of the replacement of the silyl group by hydrogen can be usefully studied using silyl derivatives-d_3, fully deuterated at the positions α to sulfur. These were synthesized, using the same procedure employed for nonlabeled compounds and starting from the tetradeutero *trans*-2-thiahydrindane sulfoxide (**2**$_{\mathbf{d4}}$) >98% pure, prepared treating **2** with 3M NaOD in D_2O.

By silylation of **2**$_{\mathbf{d4}}$ two isomers (**4**$_{\mathbf{d3}}$) and (**5**$_{\mathbf{d3}}$) were obtained, which separated and oxidized with MCPBA or reduced with $LiAlD_4$, gave the trideutero sulfones and sulfides derivatives respectively (when $LiAlH_4$ is used for reduction, the deuterium geminal to $SiMe_3$ group is partially substituted by an hydrogen, nevertheless, the $SiMe_3$ group maintains its initial configuration as can be established by ^{13}C NMR. This is not surprising because it is reported in the literature that the H-D exchange of the diastereotopic hydrogens α to sulfoxide proceeds at significantly different rates and with retention of carbanion configuration[7]).

The protiodesilylation of these compounds was achieved with tetrabutylammonium fluoride in THF. After treatment with fluoride of the silyl-d_3 derivatives in the ^1H NMR spectra of the recovered products signals appear which correspond to the entering equatorial or axial hydrogen which has replaced the silyl group. The entering proton may derive from "anhydrous" Bu_4NF, which contains 0.1-0.3 molar equivalent of water,[8] or from tri-*n*-butylamine, deriving from a β-elimination on Bu_4NF.[9]

The results of these studies, reported in Table 1, reveal several interesting trends.

Table 1 Protiodesilylation Reaction on Labelled Compounds:



Entry	X	Me_3Si conf.[a]	T° C	t(h)	% Heq	% Hax	% Des.
1	SO_2	equatorial	20	3	52	48	93
2	SO_2	axial	20	5	59	41	95
3	SO	equatorial	20	5	58	42	97
4	SO	axial	20	5	60	40	95
5	S	equatorial	20	12	91	9	40
6	S	axial	rfx	48	72-60	28-40	40

(a) The setting of the group should be considered pseudo-equatorial or pseudo-axial.

Related to reaction times two general observations emerge: 1) the desilylation occurs more rapidly in compounds with the silyl groups equatorial (entries 1, 3, 5) that in the corresponding sulfone, sulfoxide and sulfide with the silyl group axial (entries 2, 4, 6). This behaviour appears enhanced in the sulfide derivatives (entries 5 and 6); in order to obtain, in both cases, the same percentage of protiodesilylation we had to carry the reaction on the substrate with the silyl group axial for several days at the THF reflux temperature. We can assume that this behaviour results from the possibility for the desilylating agent to approach more or less easily the silyl group; 2) the times required for the desilylation decrease with the increase of the oxidation state of the sulfur atom. To confirm these results, competitive experiments were carried on an equimolecolar mixture of the sulfones (**7**) and (**9**), and analogously on a mixture of the sulfoxides (**4**) and (**5**). Subjecting separately these mixtures to conditions of time and temperature usually applied to obtain a complete desilylation of the equatorial silylated substrates, exclusively silyl derivatives axial were find in the reaction mixture, obviously together with desilylated compounds. Regarding the stereochemistry of the protiodesilylation (Table 1) we can observe that the two sulfone isomers (entries 1 and 2) *give substantially replacement of the* quasi-equatorial or quasi-axial silyl group with approximately the same percentage of inversion and retention, with a little preference for the quasi-equatorial protonation. It can be confidently affirmed that the desilylated products from the two isomers derive from the same intermediate, probably a free stabilised sulfinyl carbanion, which seems not to retain any memory of their precursor configuration. This could result from the minor reactivity of a sulfone-stabilised carbanion which could live long enough to racemise. Analogous results were obtained by desilylation of the two sulfoxides (entries 3 and 4). Consequently in the case of sulfones and sulfoxides, the protiodesilylation is substantially stereoconvergent. To exclude processes of isomerisation during the protiodesilylation we have analyzed, after only 1 h of reaction, the reaction mixture obtained by protiodesilylation. The exclusive presence of only one silyl derivative, the sulfone (**9**), clearly indicates that the F^- ions cannot produce isomerisation. For the sulfide with the silyl group quasi-equatorial (entry 5), the protiodesilylation, even if slow, was very stereoselective giving high percentage of retention (91%), while for the sulfide with the silyl group quasi-axial (entry 6) a significant percentage of retention (72-60%), together with partial inversion (28-40%), was observed. Nevertheless, in the latter case (entry 6) to obtain the 40% yield of the desilylation, due to the extreme slowness of the reaction, we had to operate at higher temperature and consequently, because of the instability of the desilylating agent at the THF reflux temperature,[9] TBAF was added at time. The reaction conditions can not, therefore, be exactly standardised and of course the results obtained with this substrate are not completely comparable to all the others cases. However, it is interesting to note that also in this latter case only the starting substrate free of appreciable axial-equatorial isomerisation can be detected. Finally the circumstance that the integral of entering hydrogen (axial and equatorial) corresponds to only one hydrogen in all the cases, can exclude the presence of other processes of epimerization, which might derive from TBAF which can be considered a strong base.[8]

In conclusion, we propose the formation of a pentacovalent negative intermediate generated by reversible addition of fluoride to silicon.[2] This intermediate can generate a carbanion, by heterolytic cleavage of the carbon-silicon bond, as in the case of sulfoxide and sulfone which can stabilize the negative charge. The carbanions quickly invert and, if captured by the electrophile, lead to a racemic mixture, as found for sulfoxides (**4**) and (**5**) and for sulfones (**7**) and (**9**). Nevertheless, relatively to compound (**8**) and to some extent even to **6**, we hypothesize that the pentacovalent negative intermediate is captured by an electrophile stereospecifically with retention of configuration, but we can not exclude completely the formation of a much less stabilized, then more reactive, sulfide derivative carbanion, able to incorporate a proton before racemisation.

On the basis of these data, the possibility of stabilizing a negative charge on the carbon carrying the silyl group influences the stereochemistry of the protiodesilylation. Due to the great interest in organic synthesis in the stereocontrolled formation of C-C bond, a thorough study regarding the stereochemistry of carbodesilylation is currently underway using this procedure mediated by sulfur, atom which allows an easy introduction of a silyl group, a control on the stereochemistry modifying its oxidation state, and which can finally be removed without difficulties.

EXPERIMENTAL

General All moisture sensitive reaction were performed in flame-dried glassware equipped with rubber septa under positive pressure of dry nitrogen. Organic extracts were dried over $CaSO_4$. Thin layer chromatography was performed on Merck Kieselgel 60 F_{254} the spots being developed at 110 °C with an aqueous solution of $(NH_4)_6Mo_7O_{24}$ (2.5%), $(NH_4)_4Ce(SO_4)_4$ (1%) in 10% H_2SO_4. Preparative liquid chromatography was performed on Merck Kieselgel 60 (0.040-0.063 mm). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 at 200 and 50.3 MHz respectively. Chemical shifts, unless otherwise specified, were measured in δ, and referenced to $CDCl_3$ (7.25 ppm for ^1H NMR and 77.20 ppm for ^{13}C NMR). Signal multiplicities were established by DEPT experiments. Solvents were reagent grade. Solvents and reagents were obtained dry as follows: tetrahydrofuran (THF) was distilled from benzophenone ketyl, CH_2Cl_2 and diisopropylamine were refluxed and distilled from CaH_2 then stored over molecular sieves (3Å).

***trans*-1-α-Trimethylsilyl-2-thiabicyclo[4.3.0]nonane 2-β-oxide (4) and *trans*-1-β-trimethylsilyl-2-thiabicyclo[4.3.0]nonane 2α-oxide (5).** To a solution of 5.71 g (0.036 mol) of **2**[4] in 12 mL of dry THF was added a solution of LDA, which was prepared adding 33.8 mL (0.050 mol) of 1.6 M *n*-BuLi to a solution of 7.6 mL (0.054 mol) of diisopropylamine in 40 mL of THF cooled at -78 °C. This mixture, maintained at -78 °C for 1 h, was added dropwise into a solution of 17.1 mL (0.14 mol) of freshly distilled trimethylchlorosilane in 170 mL of THF. After 3 h at -78 °C, the temperature was raised to 20 °C and the reaction mixture was quenched with 20% aqueous NH_4Cl and extracted with CH_2Cl_2. The extracts dried and evaporated gave a crude mixture whose ^{13}C NMR spectrum showed two sets of signals (intensity ratio 1:1), corresponding to the two isomers which could be separated by flash chromatography (silica, Et_2O/MeOH, 98/2). 0.45 g of **4** and 0.55 g of **5** for a 80% total yield were obtained as viscous colourless oils.

Spectra of compound(**4**).^1H NMR δ: 3.68 (dd, 1H, C_3H_{eq}, J = 13.27, 7.49 Hz), 2.65 (m, 1H), 2.39 (d, 1H, $H_{gem}SiMe_3$, J = 7.53 Hz), 2.20 (dd, 1H, C_3H_{ax}, J = 12.23, 13.25 Hz), 1.95 (m, 2H), 1.75 (m, 2H), 1.48 (m, 1H), 1.20 (m, 4H), 0.10 (s, 9H, $3CH_3$). ^{13}C NMR δ: 63.79 (C1), 62.71 (C3), 47.18 (CH), 45.22 (CH), 31.32, 30.99, 25.95, 25.63 ($4CH_2$), -0.23 ($3CH_3$). Anal. Calcd for $C_{11}H_{22}OSSi$: C, 57.33; H, 9.62. Found:

C, 57.31; H, 9.61.

Spectra of compound(**5**).^{1}H NMR δ: 2.88 (dd, 1H, C_3H_{eq}, J = 12.42, 4.42 Hz), 2.15 (m, 1H), 1.90 (dd, 1H, C_3H_{ax}, J = 12.48, 12.80 Hz), 1.85 (m, 1H), 1.68 (m, 2H superimposed to d, 1H, H_{gem} $SiMe_3$, J = 10.53 Hz), 1.10 (m, 6H), 0.02 (s, 9H, $3CH_3$). ^{13}C NMR δ: 66.42 (C1), 59.19 (C3), 48.57(CH), 45.11(CH), 32.38, 30.38, 25.81, 25.36 ($4CH_2$), -2.30 ($3CH_3$). Anal. Calcd for $C_{11}H_{22}OSSi$: C, 57.33; H, 9.62. Found: C, 57.34; H, 9.60.

***trans*-1-α-Trimethylsilyl-2-thiabicyclo[4.3.0]nonane (6)**. To a solution of 2.30 g (0.01 mol) of **4**, in 100 mL of dry THF, 0.76 g (0.02 mol) of $LiAlH_4$ were added. The suspension, stirred for 5 h at rt, was quenched with 5% aqueous NH_4Cl then filtered, dried and evaporated to give a crude product which was purified by flash chromatography (silica, light petroleum/Et_2O, 99.5/0.5), obtaining 1.93 g (84%) of **6** as a white oil. ^{1}H NMR δ: 2.85 (dd, 1H, C_3H_{eq}, J = 6.31, 9.85 Hz), 2.57 (d, 1H, $H_{gem}SiMe_3$, J = 8.55 Hz), 2.45 (dd, C_3H_{ax}, J = 9.85, 10.82 Hz), 1.92 (m, 2H), 1.70 (m, 2H), 1.50 (m, 1H), 1.13 (m, 5H), 0.08 (s, 9H, $3CH_3$). ^{13}C NMR δ: 51.28 (CH), 47.30 (CH), 37.42(C1), 37.21, 32.43, 31.82, 26.32, 25.65 ($5CH_2$), -1.00 ($3CH_3$). Anal. Calcd for $C_{11}H_{22}SSi$: C, 61.61; H, 10.34. Found: C, 61.63; H, 10.32.

***trans*-1-β-Trimethylsilyl-2-thiabicyclo[4.3.0]nonane (8).** Was obtained from **5** with the same procedure used for **6** obtaining a white oil with identical yield. ^{1}H NMR δ: 2.80 (dd, 1H, C_3H_{eq}, J = 9.82, 6.60 Hz), 2.25 (dd, 1H, C_3H_{ax}, J = 11.07, 10.31 Hz), 2.10 (d, 1H, $H_{gem}SiMe_3$, J = 10.99 Hz), 1.90 (m, 2H), 1.68 (m, 2H), 1.40 (m, 1H), 1.08 (m, 5H), 0.02 (s, 9H, $3CH_3$). ^{13}C NMR δ: 51.62 (CH), 50.82 (CH), 38.79 (C1), 36.53, 32.03, 31.70, 25.98, 25.74 ($5CH_2$), -2.16 ($3CH_3$). Anal. Calcd for $C_{11}H_{22}SSi$: C, 61.61; H, 10.34. Found: C, 61.59; H, 10.32.

***trans*-1-α-Trimethylsilyl-2-thiabicyclo[4.3.0]nonane 2,2-dioxide (7).** To a solution of 2.30 g (0.01 mol) of **4** in 90 mL of dry CH_2Cl_2 5.18 g (0.015 mol) of 3-chloroperbenzoic acid (50% purity) were added. After 4 h at rt the excess of peracid was quenched with 10% aqueous sodium metabisulfite, then the organic layer was extracted with saturated aqueous $NaHCO_3$, dried and evaporated, giving 2.34 g (95%) of **7** as a colourless oil. ^{1}H NMR δ: 3.14 (dd, 1H, C_3H_{eq}, J = 5.90, 12.25 Hz), 2.87 (d, 1H, $H_{gem}SiMe_3$, J = 10.01 Hz), 2.67 (dd, 1H, C_3H_{ax}, J = 12.30, 12.25 Hz), 2.24 (m, 1H), 1.88 (m, 5H), 1.30 (m, 4H), 0.25

(s, 9H, $3CH_3$). ^{13}C NMR δ: 59.66 (C3), 59.18 (C1), 46.66 (CH), 40.73 (CH), 30.86, 30.24, 26.07, 25.37 ($4CH_2$), 0.12 (CH_3). Anal. Calcd for $C_{11}H_{22}O_2SSi$: C, 53.61; H, 9.00. Found: C, 53.63; H, 9.01.

***trans*-1-β-Trimethylsilyl-2-thiabicyclo[4.3.0]nonane 2,2-dioxide (9).** The title compound was obtained as a colourless oil from **5** with the same procedure used for **7** and with identical yield. ^1H NMR δ: 3.20 (dd, 1H, C_3H_{eq}, J = 12.70, 7.20 Hz), 2.63 (dd, 1H, C_3H_{ax}, J = 12.04, 12.12 Hz), 2.18 (d, 1H, $H_{gem}SiMe_3$, J = 13.53 Hz), 1.80 (m, 6H), 1.20 (m, 4H), 0.20 (s, 9H, $3CH_3$). ^{13}C NMR δ: 60.29 (C1), 59.67 (C3), 45.63 (CH), 44.75 (CH), 30.72, 30.20, 25.65, 25.40 ($4CH_2$), -1.98 ($3CH_3$). Anal. Calcd for $C_{11}H_{22}O_2SSi$: C, 53.61; H, 9.00. Found: C, 53.59; H, 9.02.

Labelled compounds

***trans*-1,1,3,3-Tetradeutero-2-thiabicyclo[4.3.0]nonane 2-oxide ($\mathbf{2_{d4}}$).** To a 3M solution of NaOD in D_2O, under N_2, 5.86 g (0.037 mol) of **2** in 7.5 mL of CH_3OD were added. After 7 days at reflux, the mixture was cooled, neutralized with HCl conc., extracted with CH_2Cl_2 and dried. After evaporation of solvent 5.71 g (95%) of $\mathbf{2_{d4}}$ (>98% labelled α to sulfur) were obtained.

The labelled compounds ($\mathbf{4_{d3}}$) and ($\mathbf{5_{d3}}$) were obtained treating $\mathbf{2_{d4}}$ with LDA and Me_3SiCl with the same procedure used for non labelled compounds.
$\mathbf{6_{d3}}$ And $\mathbf{8_{d3}}$ were obtained from $\mathbf{4_{d3}}$ and $\mathbf{5_{d3}}$ respectively using $LiAlD_4$, $\mathbf{7_{d3}}$ and $\mathbf{9_{d3}}$ from $\mathbf{4_{d3}}$ and $\mathbf{5_{d3}}$ with 3-chloroperbenzoic acid.
In the ^1H NMR spectra of these compounds obviously there are not signals of protons α to sulfur and other signals are broad due to coupling with deuterium.
In the ^{13}C NMR spectra the signals of mono or dideuterated carbon almost disappear due to coupling with deuterium, the chemical shifts of the bridgehead carbons (α to deuterated carbons) were decreased of ~0.08 ppm.

Desilylation of α-thiasilanes.

The reaction was carried adding 10 mL of 0.1 M TBAF solution in THF to 1 mmol of compounds ($\mathbf{4_{d3}}$-$\mathbf{9_{d3}}$) for the times and temperatures reported in Table 1. The reaction mixture quenched with 5% aqueous NH_4Cl, after evaporation of THF was extracted with CH_2Cl_2. The organic layers, dried and evaporated, gave a crude mixture which was subjected to ^{1}H and ^{13}C NMR spectroscopy to estimate the percentage of desilylation (reported in Table 1). The obtained products were also separated by flash chromatography on SiO_2 using petroleum ether/Et_2O 99.5/0.5 as eluent for sulfides, Et_2O/methanol 95/5 for sulfoxides and Et_2O/methanol 97/3 for sulfones. The percentage of axial and equatorial entering proton was evaluated on these pure compounds.

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