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Axial Structure of Oxathiane Benzyl Sulfonium Perchlorate

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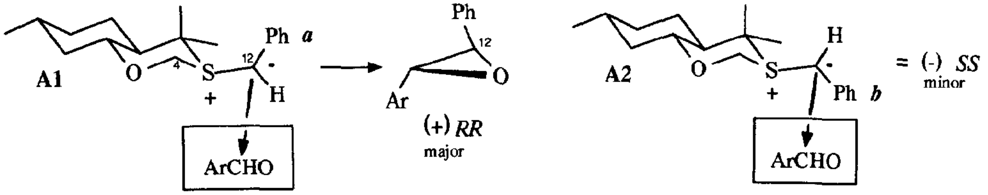
***Abstract** : It is shown that the S-benzyl substituent, in the S-benzyl sulfonium perchlorate* 2 *derived from Eliel's oxathiane, has an axial position in the solid state (X Ray analysis of a single crystal) as well as in solution (2D ^1H NMR), probably due to 1-3-anomeric effect between the lone-pairs of oxygen and sulfur.*

Introduction

During work on asymmetric synthesis of trans aromatic epoxides[1] the major (+) *RR* configuration obtained was rationalized in term of a preferred conformation, A1, of the ylide together with a sterically directed approach of the aldehyde.



Starting from the generally accepted hypothesis that, from a single sulfonium salt's isomer, only one ylide isomer having the same configuration at sulfur is formed at low temperature and because in sulfonium salts derived from six membered cyclic sulfides the third S-substituents were found equatorial[2,3], the CHPh group was, at that time, envisaged to be equatorial (conformation A1).

On the other hand, according to literature results[4-7], a 120° value was choosen for the torsional angle C4-S-C12-H (using the crystallographic numbering) ; therefore, as a consequence of the *R* absolute configuration obtained at C12 (using the crystallographic numbering), the rather hindered position ***a*** of the phenyl ring had to be considered (A1) instead of the less hindered position ***b*** (A2).

Confronted with this unexpected required conformation of the phenyl ring we decided to determine the structure of the starting sulfonium salt.

Results

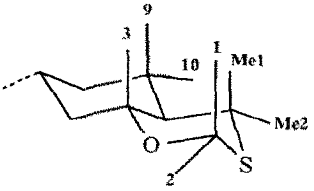
The (-) benzylic sulfonium perchlorate **2** has been obtained as a single diastereomer through alkylation of (+) oxathiane **1** at 0°C[1].

^{1}H NMR

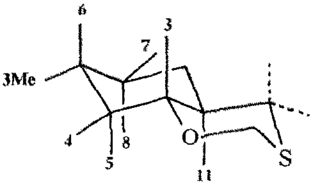
As the benzylic sulfonium salt **2** was only soluble in acetone-d6, the oxathiane **1** was also studied in this solvent. Full assignments of the ^{1}H NMR spectra of both compounds (**1** and **2**) have been done using 1D and 2D techniques.

Oxathiane **1**

In this solvent accidental equivalences lead to strong overlap of signals. However the two doublets at 5.02 ppm and 4.67 ppm (J_{12}=12 Hz) and the double triplet at 3.37 ppm ($2J_{aa}$=10 Hz, J_{ae}=4 Hz) are easily assigned to O-CH_2-S and to ^{3}H*ax* respectively.



NOESY : in bold, protons assigned using NOESY



COSY : in bold, protons assigned using COSY

Examination of the NOESY map shows that the 5.02 ppm doublet correlates to the ^{3}H*ax* signal (3.37 ppm) and to the methyl singlet (1.42 ppm). Therefore the 5.02 ppm doublet and the 1.42 ppm singlet are assigned respectively to ^{1}H*ax* and $^{1}CH_3$*ax* ; as a consequence the 4.67 ppm doublet is assigned to ^{2}H*eq*.

Moreover, the 1.42 ppm singlet ($^{1}CH_3$*ax*) correlates to the other methyl singlet (1.21 ppm, $^{2}CH_3$*eq*) and to ^{9}H*ax* (~1 ppm), then the 1.21 ppm singlet ($^{2}CH_3$*eq*) correlates to ^{10}H*eq* (1.85 ppm, multiplet).

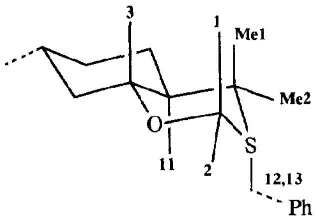
On the COSY map one can see that : the ^{3}H*ax* (3.37 ppm, double triplet) shows a cross peak to ^{4}H*eq* (1.85 ppm, narrow multiplet), to ^{11}H*ax* (1.47 ppm, multiplet) and to ^{5}H*ax* (~1.05 ppm, triplet). The ^{4}H*eq* (1.85 ppm) shows also a cross peak to ^{6}H*ax* (1.47 ppm, multiplet) and ^{6}H*ax* to $^{3}CH_3$*eq* (0.90 ppm, doublet). Then ^{7}H*eq* (1.7 ppm, multiplet) shows a cross peak to ^{8}H*ax* (~1 ppm, triplet).

The results are sumarized on Table 1

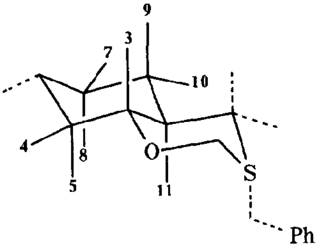
Sulfonium salt **2**

As for the oxathiane **1** some signals are easily assigned. The two doublets at 5.8 ppm and 5.1 ppm (J_{12}=12 Hz), the AB system at 5.0 ppm and the double triplet at 4.07 ppm can respectively be assigned to O-CH_2-S, to CH_2-Ph and to ^{3}H*ax*.

Examination of the NOESY map shows that the 5.8 ppm doublet correlates to the ^{3}H*ax* signal (4.07 ppm) and to one of the methyl singlet (1.9 ppm). Therefore the 5.8 ppm doublet and the 1.9 ppm singlet are assigned to ^{1}H*ax* and ^{1}CH$_3$*ax*, as a consequence the 5.1 ppm doublet is assigned to ^{2}H*eq*. Moreover the 5.0 ppm AB system(^{12}H and ^{13}H) correlates to ^{11}H*ax* (2.4 ppm, double-triplet) and to ^{2}CH$_3$*eq* (1.8 ppm, singlet) which, in turn, correlates to ^{11}H*ax* (2.4 ppm, double triplet).



NOESY : in bold, protons assigned using NOESY



COSY : in bold, protons assigned using COSY

Upon examination of the COSY map one can see that ^{3}H*ax* (4.07 ppm, double triplet) shows a cross peak to ^{11}H*ax* (2.4 ppm, double triplet) and to ^{5}H*ax* (1.4 ppm, quadruplet, $^{2}J_{45}={}^{3}J_{aa}$) which, in turn, correlates to ^{4}H*ax* (2 ppm, overlapped with the solvent signal). Then ^{11}H*ax* (2.4 ppm, double triplet) shows a cross peak to ^{9}H*ax* (1.25 ppm, quadruplet., $^{2}J_{910}={}^{3}J_{aa}$) which, in turn, correlates to ^{10}H*eq* (2 ppm, overlapped with the solvent-signal) and to ^{8}H*ax* (1.15 ppm, quadruplet , $^{2}J_{78}={}^{3}J_{aa}$). ^{8}H*ax* shows a cross peak to ^{7}H*eq* (1.8 ppm, overlapped with the two methyl-singlets).
The results are gathered in Table 1.

From these results one could conclude that in this sulfonium salt 2 the benzyl group has an axial position in solution.

Table 1 : ^{1}H chemical shifts (acetone d6) for 1 and 2.

	^{1}CH$_3$*ax*	^{2}CH$_3$*eq*	^{3}CH$_3$*eq*	^{1}H*ax*	^{2}H*eq*	^{3}H*ax*	^{4}H*eq*	^{5}H*ax*
1	1.42	1.21	0.90	5.02	4.67	3.37	1.85	1.05
2	1.9	1.8	0.90	5.8	5.1	4.07	2.0	1.4

	^{6}H*ax*	^{7}H*eq*	^{8}H*ax*	^{9}H*ax*	^{10}H*eq*	^{11}H*ax*	^{12}H,^{13}H
1	1.47	1.70	1	1	1.85	1.47	
2	1.6	1.80	1.15	1.25	2.0	2.40	5.0

X-RAY

Sulfonium salt 2

The sulfonium salt 2 was first obtained as a powder by precipitation from a CH_2Cl_2 solution using Et_2O and was then recrystallized in a 1/1 mixture of acetone and CH_2Cl_2 to give small single crystals suitable for X rays analysis.

The structure, Figure 1, ***shows that the benzyl group has indeed an axial position as suggested by the NMR studies.***

All bond distances and bond angles found are in the normal range. Some important bond distances, bond angles and torsional angles are given on Table 2.
One must notice that the phenyl ring is swept away from the gem-dimethyl substituted C1 carbon.

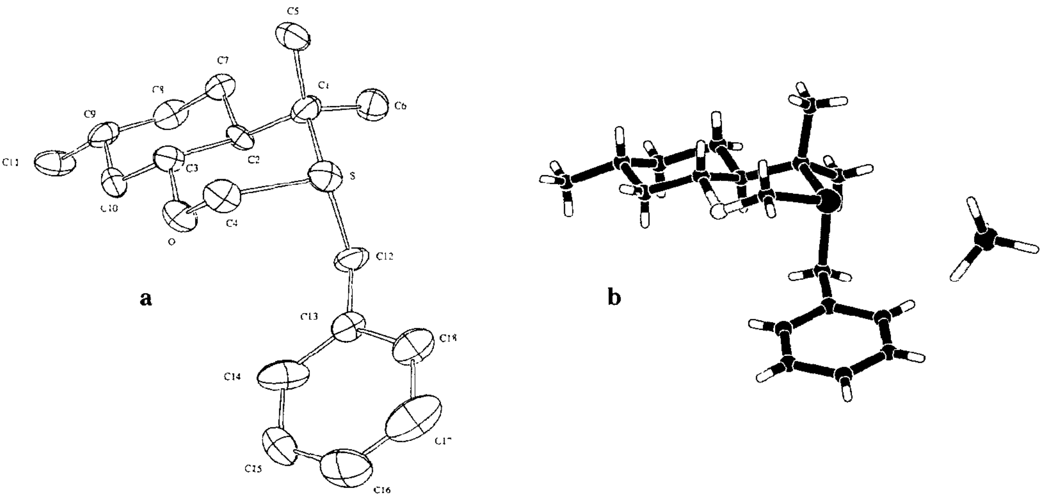


Figure 1, a : Ortep plot of one molecule of 2 showing the labeling scheme used. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted. **b** : CAP[9] stick and bond plot of one molecule of 2.

Conclusion

It appears that, in the sulfonium salt 2, the benzyl group is axial in the solid state (X ray of a single crystal) and in solution (^1H NMR/acetone d6).

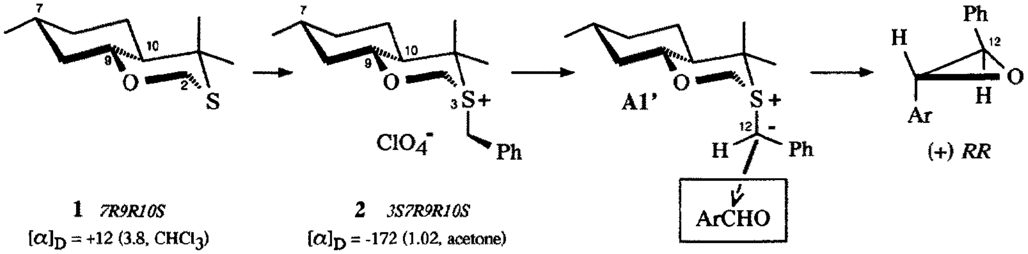
Table 2 : Some important bond distances, bond angles and torsional angles

C1-S	1.861 Å	C3-O-C4-S	-69.8°
C4-S	1.866 Å	O-C4-S-C1	+53.6°
C12-S	1.835 Å	C4-S-C1-C2	-44.0°
C3-O	1.463 Å	C7-C2-C1-S	+175.2°
C4-O	1.376 Å	C7-C2-C1-C5	+58.2°
		C10-C3-O-C4	-167.4°
C1-S-C4	99°	C2-C1-S-C12	+60.7°
C1-S-C12	105.6°	O-C4-S-C12	-54.6°
C4-S-C12	101.4°	C1-S-C12-C13	-165.2°
C2-C1-S	110.6°	C4-S-C12-C13	-61.9°
O-C4-S	110.1°	S-C12-C13-C14	+102.9°

This is the first example of a six-membered sulfonium salt having the third group at sulfur in an axial position and one could think that this is due to a 1-3- anomeric effect between one of the oxygen lone-pairs and the sulfur lone-pair.

Therefore, the formation of the ylide being conducted at 0°C,and considering that the barrier to inversion at sulfur has been determined to be around 23 Kcal/mole in ylides[8], one can postulate that no inversion occurs during the reaction and that an axial position can also be envisaged for the CHPh group in the reacting ylide.

Therefore conformation **A1'** ought to be used in our model of approach instead of **A1**. One must then notice that in **A1'** the phenyl ring does not have to be forced into a hindered position to fit the results and that the same front approach leads to the desired *R* configuration at C12.



1 *7R9R10S*
$[\alpha]_D$ = +12 (3.8, $CHCl_3$)

2 *3S7R9R10S*
$[\alpha]_D$ = -172 (1.02, acetone)

Experimental section

^{1}H NMR : Proton NMR spectra have been recorded on a Bruker AC-200, δ in ppm are refered to acetone d6 (2.05 ppm). The 2D experiments have been done using Bruker programms with the following parameters . COSY : P1 = 90°, P2 = 45°, D1 = 2s, Hz/pt = 1.6 ; NOESY : P1 = P2 = P3 = 90°, D1 = 3s, D9 = 2s, Hz/pt = 2.5 .

X-ray : One single crystal was cut out from a cluster of crystals and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of 2 belong to the orthorhombic system.

Quantitative data were obtained at -100°C achieved using a local built low -temperature device. The resulting dataset was transfered to a VAX computer, and for all subsequent calculations the Enraf-Nonius VAX[10] package was used. Three standard reflections measured every hour during the entire data collection period showed no significant trend. The data were corrected for Lorentz polarisation and absorption factors, the latter calculated from psi scans of four reflections. The structure was solved using MULTAN[11]. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coodinates (C-H = 0.95A) and isotropic temperature factors such as B(H) = 1.3 Beqv(C) A^2 but not refined. Full least-squares refinement ; $\sigma^2(F^2) = \sigma^2\text{counts} + (pI)^2$. The absolute configuration was determined by comparing x,y,z and -x,-y,-z refinements. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous distersion coefficients come respectively from ref. 12a and 12b.

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