Tetrahedron Letters No. 31, pp 2775 - 2776.
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0040-4039/78/0729-2775$02.00/0

STEREOCHEMISTRY OF 4-PHENYLTRIMETHYLENE SULFITES. A REINVESTIGATION

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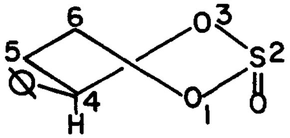
(Received in USA 17 February 1978; received in UK for publication 1 June 1978)

In 1972, the conformational analysis, by ^{1}H NMR, of a material, purported to be 4-phenyltrimethylene sulfite (below), was published.(1) This material, a liquid, was purified

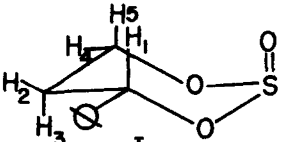


by gas chromatography and characterized only by its boiling point. It was stated that the ^{1}H NMR analysis gave results "unexpected for a chair conformation or a chair-chair equilibrium" and a twist conformation was proposed. The spectrum of the neat liquid was analyzed, although earlier it had been demonstrated(2) that trimethylene sulfites experience strong self association, are likely to be dimers at high solute concentration.

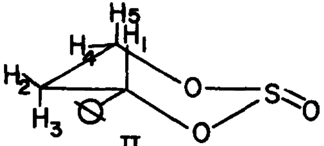
A further puzzling feature(1) was that no allusion was made to the fact that <u>two</u> isomers are possible for 4-phenyltrimethylene sulfite. We now report the synthesis of both isomers of this material and their stereochemical analysis via ^{1}H and ^{13}C NMR.

Synthesis of a mixture of the isomeric 4-phenyltrimethylene sulfites I and II, was accomplished by treatment of 1-phenyl-1,3-propanediol with $SOCl_2$ in dry ether containing excess pyridine (3). Following standard workup,(3) the mixture was chromatographed on silica gel using benzene as eluent. Initial fractions contained a liquid isomer I, n_D^{25} = 1.5458, followed by a white solid, II, m.p. 60-61^{o}C. IR spectra of I and II showed characteristic sulfinyl stretching at 1190 and 1210 cm^{-1}respectively. Both compounds gave satisfactory elemental analysis and mass spectra.

We formulate I and II as chair forms, based on ^{1}H and ^{13}C NMR data, obtained using



I



II

0.1 M solutions in $CDCl_3$, on a Varian XL-100-12 NMR spectrometer. ^{1}H spectra were analyzed via the LAOCN3 program and fitted to an RMS error of ±0.1. Phenyl regions were not analyzed. ^{1}H results are presented in Tables 1 and 2, and those for Albriktsen's material "X" are included for comparison.

Table 1. ^{1}H chemical shifts (δ from TMS ± 0.1)

Compd	H-1	H-2	H-3	H-4	H-5	φ
I	5.93	1.78	2.48	3.92	5.09	(7.30)
II	5.43	1.90	2.37	4.54	4.54	(7.40)
"X"(1)	4.99	2.12	2.29	3.29	3.48	Not reported(1)

Table 2. ^{1}H-^{1}H J's (Hz ± 0.1)

Compd	J_{12}	J_{13}	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}
I	2.6	12.5	-14.6	1.6	2.6	4.7	11.8	-12.2
II	2.7	11.5	-14.1	1.9	3.2	4.7	11.5	-12.1
"X"(1)	5.6	8.3	-14.8	6.0	4.6	5.5	9.1	-11.1

Clearly, results for our liquid isomer I are at great variance with those for the liquid "X". The differential shifts between I and II are consistent with previously noted(4) trends in chair sulfites. An axial S = 0, such as in I, deshields the syn-axial protons (H_1 and H_5) by ca 0.5 ppm relative to isomer II, where the S = 0 is equatorial. In I and II, the large vicinal couplings (J_{13} and J_{35}) indicate chair conformations, since these are typical couplings between axial protons. Also, the small couplings between potentially e-e and a-e protons are consistent with chairs. The large negative geminal J's are normal, J_{45} being more positive due to the influence of the adjacent oxygen atom. ^{13}C shifts are presented in Table 3. The upfield shifts of 9.9 and 6.6 ppm at C-4 and C-6 of I relative to II are due to the "gauche-γ" relationship(5) between the axial S = 0 and the C-4, 6 ring carbons in I. Such effects are well documented in chair conformers of thiane-oxides(6) and methylated sulfites.(5) Clearly there is no need to invoke non-chairs for either isomer of 4-phenyltrimethylene sulfite. Findings for di- and triphenylated sulfites will be reported in a full paper.

Table 3. ^{13}C NMR (δ_C from TMS ± 0.1 ppm)

					Aromatics		
Compd	C-4	C-5	C-6	quat.	o	m	p
I	68.8	33.5	58.0	138.7	126.3	128.8	127.0
II	78.7	31.8	64.6	138.3	126.1	128.7	128.3

To investigate the possibility that Albriktsen, in examining the spectrum of the neat liquid "X", was observing a polymer of our liquid isomer I, we have recorded a 60 MHz ^{1}H spectrum of neat I and compared it with the spectrum published earlier.(1) The results are drastically different and accordingly, "X" could not have been a 4-phenyltrimethylene sulphite.

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