

¹¹⁹Sn NUCLEAR MAGNETIC RESONANCE AND MASS SPECTROMETRIC STUDIES OF THE STANNYLENES
OF CHIRAL AND ACHIRAL DIOLS : AN INTERPRETATION OF THEIR REGIOSPECIFIC ACTIVATION.

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¹¹⁹Sn n.m.r., and (in some cases) mass spectrometric studies of carbohydrate-derived chiral diols, and other ones, suggested that they are dimer with C-2 symmetry in all physical states (except, may be, in polar solvents), and this may be the origin of the unique nucleophilic enhancement of one oxygen atom of the parent diols.

Stannylene derivatives of diols have proved very useful intermediates for the regioselective oxidation,¹ acylation and alkylation in polyols.² Molecular weight estimations,³ ¹¹⁹Sn chemical shifts⁴ and Mossbauer parameters⁴ have suggested the dimeric structure A for derivatives of simple glycols in solution or in the solid state, and this was further substantiated by the solid state structure determination of the dibutylstannylene of compound 1.⁵

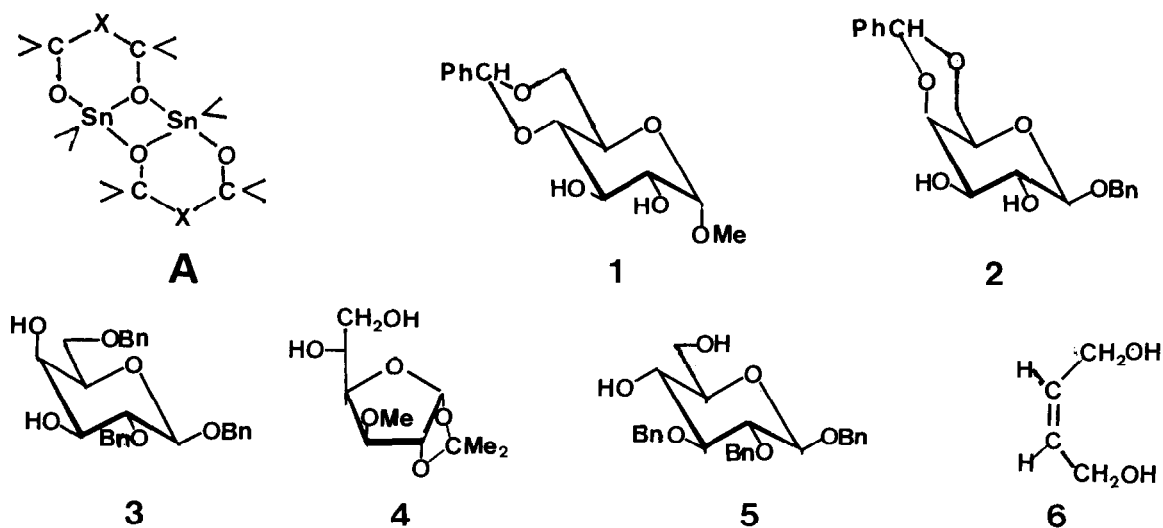
Clearly, conversion of a diol to a stannylene derivative of the type shown in expression A raises the intriguing possibility of distinguishing between the reactivities of the two oxygen atoms of the original diol. This, in turn, may explain the origin of nucleophilic enhancement specifically of one of the two oxygen atoms in such derivatives. For this reason we have investigated the generality and stability of structure A, giving specific attention to some very useful stannylene derivatives of partially protected carbohydrates.

¹¹⁹Sn n.m.r. studies (Table).

The parent diols were selected to represent different relative dispositions of hydroxyl groups, such as conformationally biased, trans diols 1 and 2, the more flexible cis diol 3, the primary-secondary diol 4, the 1-3 diol 5 and the 1-4 diol 6. At room temperature, all resonances occurred 121-180 p.p.m. upfield from the four-coordinate Me₄Sn reference (Experiments 1, 3, 12, 13, 14, 16), a range characteristic of tin with coordination higher than four.

Expansion of the coordination sphere of the tin atom by chelation to one sugar oxygen atom in a monomeric structure would involve considerable distortion and may be ruled out. In line with previous arguments,⁴ we conclude that the present stannylenes are dimeric. However, because of the chiral nature of the parent diols, we may go further. As only one resonance is observed in each of the examples studied, the two tin atoms of the dimer are in a symmetrical environment. But only C₂-symmetry is possible for the association of two chiral monomers. Thus, C₂-symmetry, around a twofold axis, first observed on the solid state structure of the dibutylstannylene of 1,⁵ may very well be a common features in stannylenes of diols in general.

In the liquid state, the open chain analogue, Bu₂Sn(OCHMe₂)₂ is a mixture of monomer and dimer : as the proportion of monomer increases with increasing temperature, the δ was reported



to change dramatically from -90 (at 30°C) to -34 p.p.m. (at 79°C).⁴ On the other hand, variable temperature measurements with the stannylene derived from 2 indicated a negligible change of δ in this interval, and only a 6 p.p.m. decrease from -53 to $+67^\circ\text{C}$ (experiments 2 to 5). The 7-membered ring stannylene of 6 also exists as a stable dimer in these conditions (experiments 15 and 16), so that the valency angle at tin lies in the vicinity of 90° and possibly much less.

Stannylenes are often used in polar solvents (see, however⁶) to which they may be associated as pentacoordinated monomeric units. Addition of increasing quantities of pyridine to the chloroform solution of the stannylene of 2 only changed slightly the position, but not the shape of the thin resonance line (3 Hz at half height). However the width increased to several hundred Hz in pure pyridine or dimethylformamide, with not much change in average position (Experiments 6 to 11), an indication of strong interactions in these conditions.

Mass spectrometry studies.

Some stannylenes, reported as monomeric, were too poorly soluble for n.m.r. studies: the derivatives of cis- and trans-cyclohexanediol were examined by field desorption mass spectrometry. In both cases, clusters of more than 30 peaks, centered on the mass number 692 of the most abundant $|^{118}\text{Sn}|$ -dimer were observed (there are 9 natural tin isotopes, allowing for 36 Sn_2 molecular species). No peaks reflecting the presence of monomeric species were observed. Therefore the dimeric structures of these crystalline stannylenes are still persistent in the vapour state.

Chemical ionization (NH_3 -isobutane) m.s. gave similar spectra for both cis and trans cyclohexanediol stannylenes (Figure). Peaks with mass numbers reflecting the presence of dimeric and monomeric species were found, but the second ones may correspond to an open-chain, strainless isomer. A number of peaks of intermediate masses suggests progressive stripping of the dimer rather than severance of bonds in the Sn_2O_2 parallelogram.

No signal was observed by field desorption m.s. of the stannylenes of adenosine and uridine and no dimer peak on chemical ionization, as in previously reported electron impact studies.² Mossbauer spectroscopy suggested that tin is five-coordinate in the first one.⁷

Table. ^{119}Sn Chemical Shifts in Dibutylstannylene Derivatives.^a

Experiment Nr	Parent diol	Solvent(s) (perdeuterated)	Temperature °C	δ
1	1	chloroform	24	-125.4 ^b
2	2	chloroform	-53	-149.1
3	2	chloroform	24	-145.1
4	2	chloroform	47	-144.1
5	2	chloroform	67	-143.0
6	2	chloroform-pyridine, 1:1 ^c	-40	-154.5
7	2	chloroform-pyridine, 1:1 ^c	24	-147.0
8	2	chloroform-pyridine, 1:1 ^c	60	-146
9	2	chloroform-pyridine, 1:3 ^c	60	-151
10	2	pyridine	26	-138.2 to -158.3
11	2	dimethylformamide	26	-157 (broad, $\Delta H_{\frac{1}{2}}^1$ 560Hz)
12	3	chloroform	24	-125.6
13	4	chloroform	24	-121
14	5	chloroform	24	-180
15	6	chloroform	-53	-151.6
16	6	chloroform	24	-150.8

^aMeasurements were made with a Bruker WH90 spectrometer at 33.55 MHz with $\text{Me}_4^{119}\text{Sn}$ as internal or external reference (with the same results), and proton uncoupling; the signals appeared as thin singulets ($\Delta H_{\frac{1}{2}}^1$ ca 3Hz, or 0.1 p.p.m., that 1/600 the total range); ^bRef.5; ^cby volume.

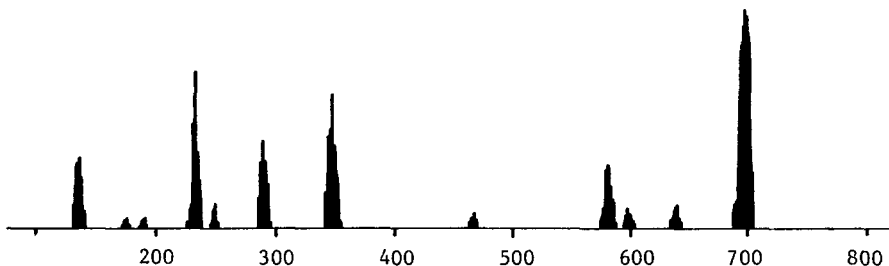


Figure. Chemical ionization (NH_3 -isobutane) m.s. fragmentation of the dibutylstannylene of trans-cyclohexanediol. Source temperature 150°C. Ionization potential 170 eV.

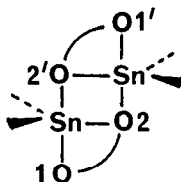
Finally, structures found in recent reports, with a ten-membered ring,⁸ or a chelate bridge between tin and the anomeric oxygen,⁹ may be ruled out, the former because ^{119}Sn n.m.r. shows that tin is five-coordinate,⁴ and the second because it would involve extreme strain and could not account for the ^{119}Sn - ^{117}Sn coupling found for the stannylene of 1 in solution.⁵

Conclusion.

To date, stannylene have only been observed as dimers with C-2 symmetry in all physical states (except, may be, when dissolved in polar solvents). The driving forces to dimerization are the two electronegative substituents at tin and (when present) the five-membered ring. The consequence of the length of the tin covalent radius is that in any conformation of this ring, "normal" angles at carbon or oxygen involve a very small angle at tin which can only be achieved with d orbitals participation. Still, dialkyldialkoxytins and stannacyclopentane may be observed

as monomers,^{4,10} so neither of these two driving forces can preclude the existence of monomeric species when acting alone.

Within one monomeric unit of the dimer, tin binds apically to one oxygen atom of the parent diol and equatorially to the other oxygen atom. Most likely, that oxygen atom of one unit acting as a ligand to the tin atom of the other one will bind apically to it. In fact, the idealized bonding scheme shown below has been confirmed by X-rays in one case.⁵



The regiospecific reactions of stannylenes with acylating and alkylating agents can be nicely explained assuming preferential rupture of the apical tin-oxygen bonds, Sn-O(1) and Sn-O(1') while O(2) and O(2') are relatively protected by threefold coordination. Possibly the tin atoms act as channels for electron shifts towards O(1) and O(1'), thus activated at the expense of O(2') and O(2) respectively.

The orientation of attack will depend upon which oxygen atom of the diol will preferentially bind apically. This may be the more electronegative, as it is known that in trigonal bipyramid complexes, electronegative ligands are more stable on apical positions. Conversion to stannylene would thus accentuate small electronegativity differences between the two oxygen atoms of a diol. But steric factors may also play, such as the change of volume of the equatorial oxygen when it loses electron density by complexation, or the steric hinderance of the butyls.

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