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Stannylated 2,3-*O*-Isopropylidene-β-D-ribofuranose Derivatives

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The structures of methyl 5-deoxy-2,3-*O*-isopropylidene-5-*C*-R_3Sn-β-D-ribofuranosides (**3**), [5-*O*-(methyl 2,3-*O*-isopropylidene-β-D-ribofuranosyl)methyl]$_n$R$_m$R$'_{(4-m-n)}$ stannanes (**4**) and 3-triphenylstannylpropyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**5**) have been investigated.

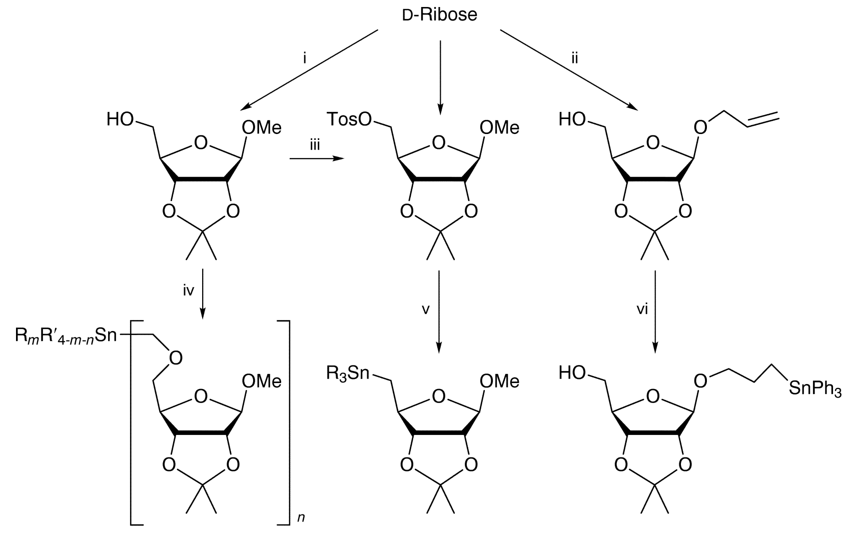
Much interest has been shown in furanose ring conformations of carbohydrates in solution and the solid state.[1–4] Ribofuranosyl rings, in general, have attracted attention as a consequence of their presence in nucleosides and nucleotides; particularly well studied have been 2,3-unsubstituted β-D-ribofuranosyl derivatives[2–4] and their 2-deoxy analogues. The more rigid 2,3-*O*-isopropylidene-β-D-ribofuranosyl derivatives **2** have attracted less, but still significant, attention.[9,10] We have investigated the solution structures of **3** ($R = Ph$ or Me), **4** ($R = R' = Ph$ or Bu, $n = 1$; $R = R' = Ph$, $n = 2$ or 3; $R = Ph$, $R' = Me$, $m = 1$ or 2, $n = 1$) and **5**, as well as the crystal structures of **3** ($R = Ph$) and **4** ($R = R' = Ph$, $n = 1$). The synthesis of **3**–**5** are shown in Scheme 1.

Crystal Data for **3** ($R = Ph$).—$C_{27}H_{30}O_4Sn$, $M_r = 537.2$, $F(000) = 548$, triclinic, $a = 9.480(4)$, $b = 10.586(4)$, $c = 14.134(9)$ Å, $\alpha = 104.98(4)$, $\beta = 105.41(4)$, $\gamma = 99.83(4)°$, $V = 1279(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_x = 1.395$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 1.028$ mm^{-1}. The data were collected at 298 K on a Nicolet P3 diffractometer using monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). The final R value was 0.053 ($R_w = 0.061$).

Crystal Data for **4** ($R = R' = Ph$, $n = 1$).—$C_{28}H_{32}O_5Sn$, $M_r = 567.3$, $F(000) = 1160$, orthorhombic, $a = 9.187(8)$, $b = 12.801(13)$, $c = 22.899(17)$ Å, $V = 2693(4)$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_x = 1.399$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.98$ mm^{-1}. The data were collected at 298 K on a Nicolet P3 diffractometer using monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). The final R value was 0.067 ($R_w = 0.050$).

The two independent molecules in the asymmetric cell of solid (**3**; $R = Ph$) are shown in Fig. 2. The difference between the two molecules concerns the orientation of the triphenylstannyl unit relative to the furanose oxygen: the furanose ring conformations in both molecules are, however, similar. The tin atom in each molecule has a distorted tetrahedral geometry with bond angles at tin varying from 106.3(4) to 114.5(4)° in molecule 1 and from 103.0(4) to 118.3(4)° in molecule 1A. The ^{119}Sn and ^{13}C solid state NMR spectra also indicate the presence of two molecular arrangements. The differences between the solution $\delta(^{119}\text{Sn})$ value (−109.6) and the solid state $\delta(^{119}\text{Sn})$ values (−81.9 and −96.3: mean −89.1) are taken to be simply a medium effect: the values are as expected for four-coordinate (alkyl)Ph_3Sn species.

The one independent molecule in the asymmetric unit of **4** ($R = R' = Ph$, $n = 1$) is shown in Fig. 5. The geometry about tin is distorted tetrahedral with bond angles at tin between 106.1(4) and 112.8(5)°: although the Sn—O(5) bond length is short [2.897(10) Å], the bond angles at tin and the $\delta(^{119}\text{Sn})$ NMR solid state value (−135.9) indicate that a significant Sn—O interaction is absent. The $\delta(^{119}\text{Sn})$ value for **4** ($R = R' = Ph$, $n = 1$) scarely changes on dissolution (−142.9 to −135.9).



4 **3** **5**

Scheme 1 *Reagents*: i, MeOH, Me_2CO, H_3O^+; ii, $H_2C{=}CHCH_2OH$, Me_2CO, H_3O^+; iii, TosCl, py; iv, R$_m$R$'_{4-m-n}$Sn(CH$_2$I)$_n$, NaH; v, R_3SnLi; vi, Ph_3SnH, AIBN

Puckering parameters[2] for the furanose rings in solid **3** ($R = Ph$) ($P = 284.4°$; $\tau_m = 36.2°$ in molecule 1; $P = 279.9°$; $\tau_m = 30.70°$ in molecule 1A) correspond to conformations

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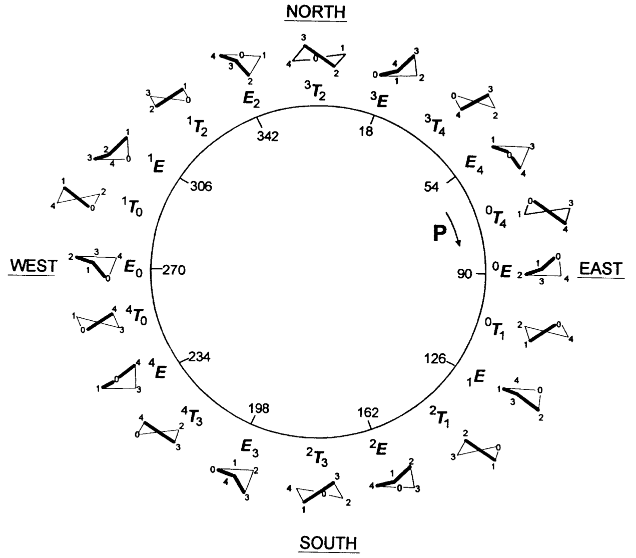

Fig. 1 Pseudorotational cycle of furanose rings showing the ten envelope (E) and ten twist (T) conformations

close to $^1T_0$ on the side towards E_0 (*i.e.* just to the north of the west point on the pseudorotational cycle), see Fig. 1.[5] The solid state conformation of the furanose ring in **4** ($R = R' = Ph$, $n = 1$) is also near $^4T_0$ [$P = 257.4°$; $\tau_m = 31.5°$].[5]

Kline and Serianni calculated values of ^3J(HH) from phase angle P and puckering amplitude τ_m values;[4b] using their graphical plots, with values for τ_m and P of 33 and 282°, respectively, values of $^3J(H^1H^2)$, $^3J(H^2H^3)$ and $^3J(H^3H^4)$ for **3** (R = Ph) were calculated to be *ca.* 1.5, 7.8 and 1.0 Hz, respectively. Essentially the same ^3J(HH) values were calculated for **4** ($R = R' = Ph$, $n = 1$). These solid state values are close to the values of 0–0.5, 6.0–6.5 and 0–1.6 Hz, respectively, directly measured in solution: thus no significant change in conformation results on dissolution. Similar conformational equilibria in solution are indicated for the furanose rings in all molecules, **3**–**5**, by the similar ^3J(HH) values; the stannyl substituents have little influence on the solution conformations. The solution conformation equilibria[9a] for **3**–**5** is considered to be $^4E \rightleftharpoons {}^4T_0 \rightleftharpoons E_0 \rightleftharpoons {}^1T_0 \rightleftharpoons {}^1E$.

Complete ^{1}H, ^{13}C and ^{119}Sn NMR solution spectra of the (iodomethyl)stannane precursors of **4** have been obtained. The $\delta(^{119}\mathrm{Sn})$ values of $\mathrm{Ph}_{4-n}\mathrm{Sn(CH_2I)}_n$ increase with n, *i.e.* −120.0, −104.4, −80.4 and −47.7 for $n = 1$–4; in contrast, $\delta(^{119}\mathrm{Sn})$ values for **4** ($R = R' = Ph$) exhibit a minimum value at $n = 2$.

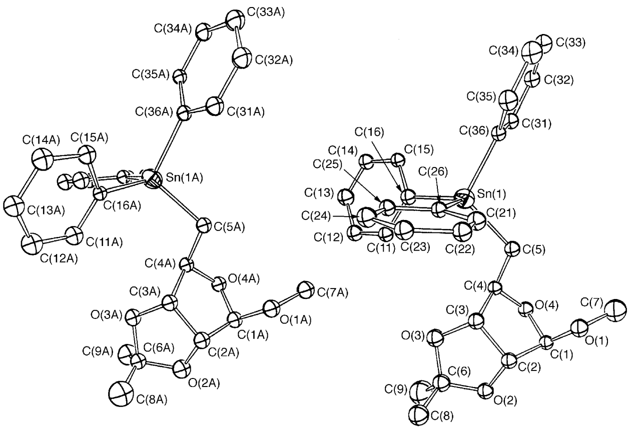

Fig. 2 The two independent molecules of **3** (R = Ph) showing the atom numbering scheme. Atoms are represented by 40% probability ellipsoids. Hydrogen atoms have been omitted

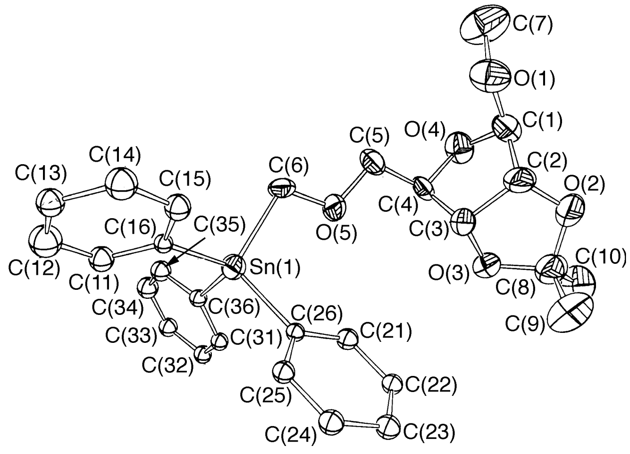

Fig. 5 The atom numbering scheme for **4** ($R = R' = Ph$, $n = 1$). Atoms are represented by 40% probability ellipsoids. Hydrogen atoms have been omitted

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Techniques used: ^{1}H, ^{13}C and ^{119}Sn solution NMR, ^{13}C and ^{119}Sn solid state NMR, X-ray crystallography, MS, IR

References: 44

Tables: 6 (NMR; selected bond lengths & angles and torsional angles; crystal data)

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References cited in this synopsis

1 V. N. Bartenev, N. G. Kamenva and A. A. Lipanov, *Acta Crystallogr., Sect. B*, 1987, **43**, 275; M. Remin, *J. Biomol. Struct. Dyn.*, 1988, **6**, 367; I. A. Il'cheva, N. G. Esipova, V. G. Tumanyan, B. P. Gottikh and V. L. Florentev, *Bioorg. Khim.*, 1989, **15**, 800; J. Jimenez-Barbero, M. Bernabe and M. Martin-Lomas, *Tetrahedron*, 1988, **44**, 1441.
2 C. Altona and M. Sundaralingam, *J. Am. Chem. Soc.*, 1972, **94**, 8205; 1973, **95**, 2333.
3 C. A. Podlasek, W. A. Stripe, I. Carmichael, M. Shang, B. Basu and A. S. Serianni, *J. Am. Chem. Soc.*, 1996, **118**, 1413 and references therein.
4 (*a*) A. S. Serianni and R. Barker, *J. Org. Chem.*, 1984, **49**, 3292 and references therein; (*b*) P. C. Kline and A. S. Serianni, *J. Am. Chem. Soc.*, 1990, **117**, 7373.
5 S. Cros, C. Herve du Penhoat, S. Perez and A. Imberty, *Carbohydr. Res.*, 1993, **248**, 81; M. Smith and C. D. Jardetzky, *J. Mol. Spectrosc.*, 1968, **28**, 70.
9 (*a*) E. J. Freyne, R. A. Dommisse, J. A. Lepoivre and F. C. Alderweireldt, *J. Carbohydr., Nucleosides, Nucleotides*, 1980, **7**, 263; (*b*) D. W. Jones, T. T. Mokoena, D. H. Robinson and G. Shaw, *Tetrahedron*, 1981, **37**, 2995; (*c*) H. Ohrui and S. Emoto, *J. Org. Chem.*, 1977, **42**, 1951; (*d*) V. A. Timoshchuk, T. M. Ermolenko and A. A. Akhrem, *J. Org. Chem., USSR*, 1988, **24**, 1092; (*e*) A. Gaudemer, F. Nief, R. Pontikis and J. Zylber, *Org. Magn. Reson.*, 1977, **10**, 135.
10 D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746; F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 1, 31.