Sterically Hindered Organometallics. Synthesis of Four-membered Rings containing Tin, Oxygen, and Sulphur. The Crystal Structure of 2,2,4,4-Tetra(2,4,6-tri-isopropylphenyl)-1-oxa-3-thia-2,4-distannetane

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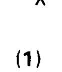
Reaction of $Na_2S{\cdot}9H_2O$ with 1,1,2,2-tetra(2,4,6-tri-isopropylphenyl)-1,2-dibromoditin in air yields the sterically hindered four-membered 1-oxa-3-thia-2,4-distannetane ring, which is a distorted rhombohedron containing distinct Sn–S [243.9(4), 243.5(4) pm] and Sn–O [204.2(8), 202.6(8) pm] bonds; the same reagents react under anaerobic conditions to yield the corresponding 1,3-dithia-2,4-distannetane, suggesting a three-membered 1-thia-2,3-distannirane as the common intermediate in the two reactions.

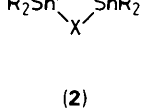
Three- and four-membered homo- and hetero-cyclic rings have received increasing attention in recent years, owing to the unusual reactivity possessed by such strained systems. For the Group 14 elements several recent reports have dealt with the characterisation of these classes of compound for silicon[1] and germanium,[2] but for the heavier element tin only the homocyclic tristannirane (**1**; X = SnR_2; R = 2,6-$Et_2C_6H_3$)[3] is known of the three-membered rings. In the case of four-membered ring systems, several are known for tin in oxidation state +2,[4] while for organotin(IV) species a limited number of symmetrical structures (**2**; X = Y = S,[5,6] Se,[5] $Bu^t{}_2Sn$[7]) have been reported. In particular, discrete four-membered rings containing oxygen are unknown save for the ubiquitous case of dimeric stannoxanes (**3**); larger rings,[3,8] or more commonly polymers,[9] are the norm. We now report structural characterisation of the first distannetane containing mixed chalcogenides (**2**; X = O, Y = S) and indirect evidence for the *in situ* formation of the first heterocyclic distannirane (**1**; X = S).

A solution of $Na_2S{\cdot}9H_2O$ (11 mmol) in water was added to a solution of 1,1,2,2-tetra(2,4,6-tri-isopropylphenyl)-1,2-dibromoditin (4 mmol) in ethanol/toluene (2:1), the mixture refluxed for 48 h and, after solvent removal, the resultant solid partitioned between toluene/water. The organic phase yielded the title distannetane (**2**; X = O, Y = S), which was purified by recrystallisation from ethanol/hexane (27%).†

The structure‡ of the distannetane (Figure 1) consists of a rhombohedral core distorted into an arrowhead arrangement by the distinct Sn–S [243.9(4), 243.5(4) pm] and Sn–O [204.2(8), 202.6(8) pm] bonds, and the differing bond angles at the bridging chalcogen [80.6(1) and 101.7(4) at S and O respectively].



(1)



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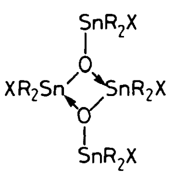
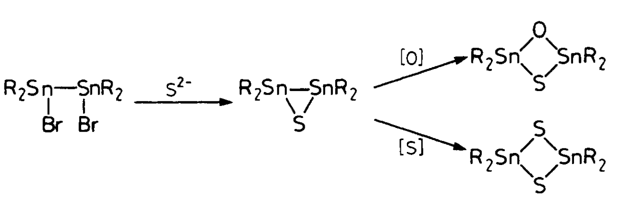


(3)

When the same reagents react in 1:1 stoicheiometry under anaerobic conditions, the product is almost exclusively the 1,3-dithia-2,4-distannetane (**2**; X = Y = S) ($\delta^{119}Sn$: −48.2 p.p.m.) with less than 2% of the 1-oxa-3-thia-2,4-distannetane ($\delta^{119}Sn$: 11.4 p.p.m.), compared to an 8:92 ratio of the same compounds produced in the synthesis under aerobic conditions described above. Since, given the aerobic stability of the dihalogenoditin precursor, it is highly unlikely that the first step in these reactions is insertion into the Sn–Sn bond to yield



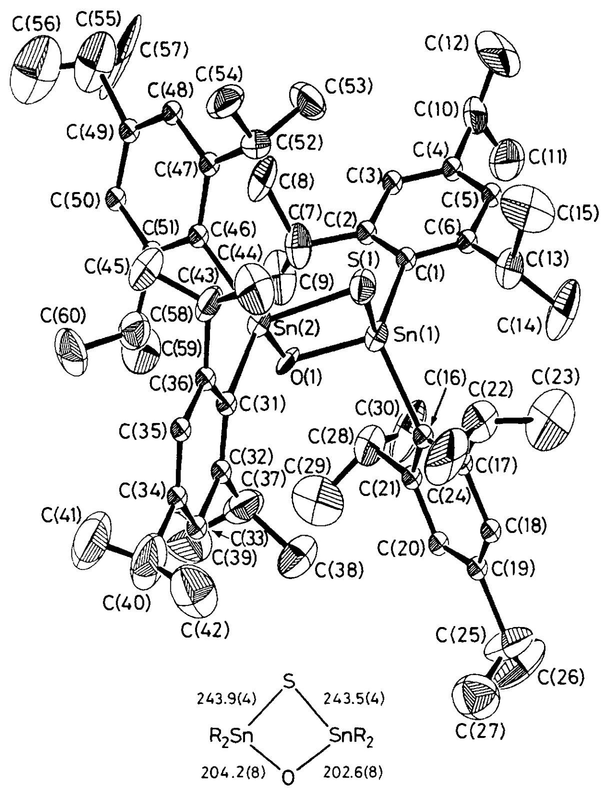


Figure 1. The structure of 2,2,4,4-tetra(2,4,6-tri-isopropylphenyl)-1-oxa-3-thia-2,4-distannetane (**2**; X = O, Y = S) showing atomic labelling. Bond distances (pm) within the central heterocycle are shown in the schematic representation.

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† All compounds gave satisfactory C and H analyses and have been fully characterised spectroscopically.

‡ *Crystal data*: $C_{60}H_{92}OSSn_2$, M = 1098.84, monoclinic, space group $P2_1/n$, a = 14.383(4), b = 21.031(4), c = 20.562(7) Å, β = 91.845(2)°, U = 6216.67 Å^3, Z = 4, D_c = 1.17 g cm^{-3}, $F(000)$ = 2304, $\mu(\text{Mo-}K_\alpha)$ = 7.90 cm^{-1}, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å. Data were collected on a Hilger and Watts Y290 four-circle diffractometer at room temperature in the range $2 < \theta < 22°$. Of the 8689 reflections collected 3806 were unique and had $I > 3\sigma(I)$, yielding final R = 0.0665 and R_w = 0.0663. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

linear distannoxanes or distannthianes, the results suggest that the reaction pathway proceeds *via* the hitherto unknown 1-thia-2,3-distannirane (**1**; X = S), with subsequent competitive oxidation with either O or S across the Sn–Sn bond.

The facile nature of this ring expansion no doubt arises as a consequence of the strain inherent in the distannirane ring, and the relief of steric crowding across the Sn–Sn bond. The dominance of O over S for insertion into the Sn–Sn bond probably results from its ability to penetrate the hydrocarbon sheath protecting the metals better than the larger, heavier chalcogen. However, these results suggest that with a reagent which can deliver nucleophiles in a more controlled way to the dihalogenoditin, *e.g.* $(Me_3Si)_2X$ (X = S, Se, PR *etc.*), the heterocyclic distannirane is a viable synthetic target. We are currently exploring this assertion.

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