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Preliminary communication

Organotin biocides

XIV *. Synthesis of new organotin heterocycles from thermal cyclisation of organotin tetrazoles. Crystal structure of 2,3,4,5-tetraaza-6-diphenylstannyl[3.4]bicyclonona-1,3-diene

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Abstract

2-(Tributylstannyl)-5-(3′-triphenylstannylpropyl)tetrazole undergoes a thermal cyclisation to yield 2,3,4,5-tetraaza-6-diphenylstannyl[3.4]bicyclonona-1,3-diene, the first of a new class of bicyclic organotin heterocycles.

We have been interested for some time in the synthesis of novel organotin compounds in which one of the hydrocarbon groups linked to tin is a C-bonded heterocycle [1]. We and others have found that compounds of type $R_3R'Sn$ are often unstable with respect to aerobic cleavage of the tin–heterocycle bond, e.g. those with R′ = imidazole, benzothiazole, or benzoxazole [1–3], but this instability can be mitigated by the inclusion of an alkyl chain between the two units i.e. $R_3Sn(CH_2)_nR'$ [4]. As part of our programme in this area we sought to prepare compounds of this type in which R′ = tetrazolyl, using the established ring building reactions described by Sisido et al. [5]. Thus, when (3-cyanopropyl)triphenyltin and tributyltin azide were heated together neat for 3 h at 140 °C the initial product was the expected 2-(tributylstannyl)-5-(3′-triphenylstannylpropyl)tetrazole (I). However, prolonged heating at the same temperature for 21 h resulted in a further cyclisation to II, with elimination of Bu_3SnPh. Similar results were obtained when the corresponding 5-(2′-triphenylstannylethyl)tetrazole precursor was used.

The conditions necessary for the formation of the bicyclic product depend on the ease of cleavage of the bond between tin and the leaving group that is part of the pendant 5-organostannylalkyl moiety. For example, in reactions paralleling that

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* For Part XIII of this series, see ref. 1.

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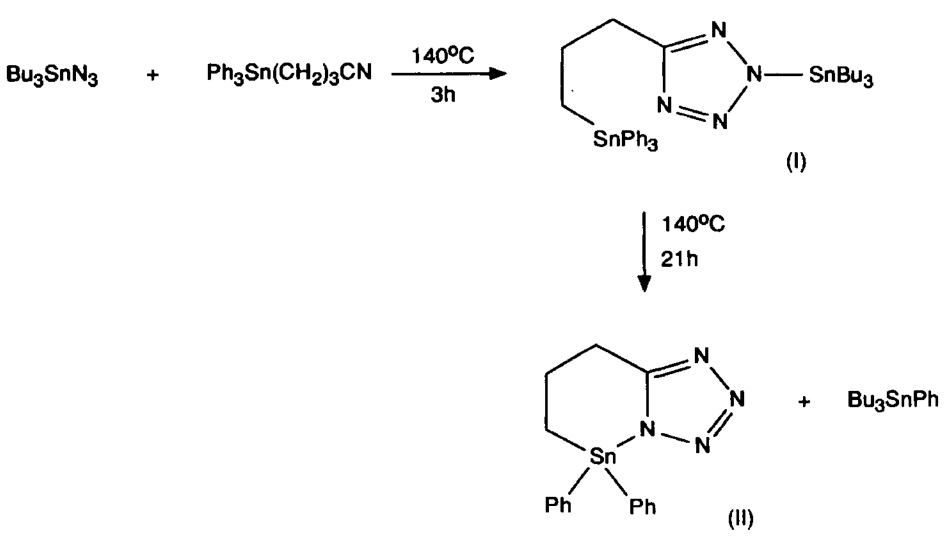

above, 5-(2′-tributylstannylethyl)tetrazoles for which elimination of Bu_4Sn is required do not cyclise even under forcing conditions, while 5-[2′-(bromodiphenylstannyl)ethyl]tetrazoles which undergo elimination of Bu_3SnBr, form the desired product in 5 min at 140 °C.

The structure of II has been confirmed crystallographically *. The geometry about tin is trigonal bipyramidal, with equatorial hydrocarbon groups and nitrogens of the tetrazole ligand in apical sites (Figure 1). Of the two axial ligands, one nitrogen arises from intramolecular chelation of the 5-alkyltetrazole to yield the bicyclic structure, the other by intermolecular coordination to give a 1-*d* polymeric array.

These results indicate that the nucleophilicity of the tetrazole nitrogens, which is usually considered to be low [6], is enhanced by the presence of a tributyltin group, and furthermore such species should be capable of reaction with a variety of electrophilic substituents suitably oriented from the 5-position of the tetrazole to yield a range of new polycyclic inorganic and organic heterocycles.

Experimental

Tributyltin azide [7] and (3-cyanopropyl)triphenyltin [8] were prepared by published methods. (3-Cyanopropyl)diphenyltin bromide was prepared by the stoichiometric reaction of (3-cyanopropyl)triphenyltin and bromine in chloroform.

Synthesis of II, Method A. Tributyltin azide (0.73 g, 2.2 mmol) and (3-cyanopropyl)triphenyltin (0.92 g, 2.2 mmol) were placed in a round-bottomed flask and heated together at 140 °C for 21 h during which the mixture solidified. The solid material II was washed with diethyl ether (4 × 50 ml) and recrystallised from $MeOH/CS_2$ (10/1) as white needles (0.64 g, 76%, m.p. 310 °C dec.). The ether

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* *Crystal data*: $C_{16}H_{16}N_4Sn$, $M = 383.0$, monoclinic, a 14.544(3), b 13.267(7), c 17.147(4) Å, β 109.63(1)°, U 3116.36 Å^3, $Z = 8$ (two molecules per asymmetric unit), $F(000) = 1520$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 15.01 cm^{-1}, space group $P2_1/c$. 2844 unique reflections with $I > 3\sigma(I)$ were used in refinement calculations in which only the tin and nitrogen atoms were allowed to vary anisotropically. Final convergence was at $R = 0.065$. Data were corrected for Lorentz, polarisation, and absorption effects.

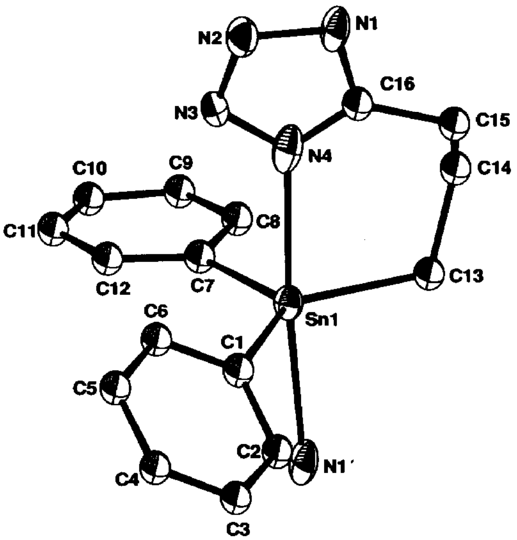

Fig. 1. Part of the polymeric structure of II. Selected geometric parameters (average of data for two independent molecules in the asymmetric unit): Sn–N4 234(2); Sn–N1′ 236(2) pm; < N1′–Sn–N4 173.4°.

washings were combined, reduced in volume and vacuum distilled (116°C, 0.3 mmHg) to yield Bu_3SnPh (0.69 g, 85%).

Synthesis of II, Method B. (3-Cyanopropyl)diphenyltin bromide (0.48 g, 1.1 mmol) and tributyltin azide (0.37 g, 1.1 mmol) were heated together in a round bottomed flask at 140°C for 5 min during which the mixture solidified. Work-up as above gave II (0.42 g, 96%) and Bu_3SnBr (0.39 g, 96%, b.p. 100°C/0.3 mmHg). Anal.: Found: C, 50.20; H, 4.37; N, 14.60. $C_{16}H_{16}N_4Sn$ calcd.: C, 50.17; H, 4.21; N, 14.62%. ^1H NMR: 7.80–7.30 (m, 10H), 2.92 (m, 2H), 2.15 (m, 2H), 1.90 (m, 2H); ^{119}Sn NMR (DMSO solution): −224.3 ppm with respect to Me_4Sn; ^{119}Sn Mössbauer data: IS 1.29, QS 3.26 mm s^{-1}.

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