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NOTE

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V*. *N*-(TRIALKYLSTANNYL)SULPHONAMIDES

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It is known that the azeotropic dehydration of a mixture of a bis(trialkyltin) oxide and the amide of a carboxylic acid often leads to the formation of the corresponding *N*-(trialkylstannyl)amido compound (eqn. 1)[2].

$$(R_3Sn)_2O + 2\,R'NH{-}CO{-}X \xrightarrow[(X=H,\,Me,\,OMe)]{-H_2O} 2\,R_3Sn{-}NR'{-}CO{-}X \qquad (1)$$

We now report that this reaction can be extended to give a simple route to *N*-(trialkylstannyl)sulphonamides (eqn. 2) which previously have been described only briefly. Mack and Parker[3] prepared *N*-(tributylstannyl)-*N*-ethyl-*p*-toluenesulphonamide from tributyltin chloride and the sodium salt of the sulphonamide, and Van der Kerk and Luijten[4] obtained *N*-(triethylstannyl)methanesulphonamide by a similar reaction, and *N*-(triethylstannyl)-*p*-toluenesulphonamide by treating triethyltin hydroxide with the sulphonamide. The properties of these compounds were not reported.

$$(R_3Sn)_2O + 2\,R'NH{-}SO_2{-}R'' \xrightarrow{-H_2O} 2\,R_3Sn{-}NR'{-}SO_2{-}R'' \qquad (2)$$

The reactions were carried out by heating the sulphonamide and bis(tributyltin) oxide in the azeotroping solvent (usually toluene) under reflux, with a Dean and Stark trap to remove water. Reaction times were usually between 1 and 3 hours, but sulphanilamide had to be heated in xylene for 2.5 hours before all the water was removed.

The products were usually purified by distillation but the tributylstannyl derivative of sulphanilamide decomposed on heating, and was purified by repeated washings with dry pentane. This compound was also anomalous in that it had no sharp melting point, and was only slightly sensitive to atmospheric moisture.

Physical properties of the stannylsulphonamides are given in Table 1. The infrared and NMR spectra are consistent with the *N*-stannyl structures which are shown, but do not preclude the possibility of *O*-stannylation, or the association of

* For Part IV see ref. 1.

TABLE 1

N-(TRIBUTYLSTANNYL)SULPHONAMIDES

	$R_3Sn-NR'-SO_2-R''$	B.p./mm	M.p.	Analysis, found (calcd.)%		
				C	H	N
1	$Bu_3Sn-NPh-SO_2-Me$	157–158°/0.01		49.4 (49.5)	7.6 (7.6)	3.2 (3.0)
2	$Bu_3Sn-NPh-SO_2-Ph$	212/0.5	29–31°	55.1 (55.2)	6.9 (7.1)	3.0 (2.7)
3	$Bu_3Sn-NPh-SO_2-C_6H_4Me$-4	208–210/0.1	38–41	56.2 (56.0)	7.5 (7.3)	2.8 (2.6)
4	$Bu_3Sn-NPr-SO_2-Me$	154–156/0.1		44.9 (45.1)	8.8 (8.7)	3.4 (3.3)
5	$Bu_3Sn-NPr-SO_2-Ph$	194–196/0.2		52.5 (51.6)	8.3 (8.0)	2.9 (2.9)
6	$Bu_3Sn-NPr-SO_2C_6H_4Me$-4	210–212/0.3		52.3 (52.6)	8.5 (8.2)	2.9 (2.8)
7	$Bu_3Sn-NH-SO_2-Ph$	220/0.5	43–46	48.5 (48.0)	7.5 (7.3)	3.1 (3.1)
8	$Bu_3Sn-NH-SO_2-C_6H_4(NH_2)$-4		80–100	47.0 (46.9)	7.2 (7.4)	6.2 (6.1)

the tin with two functional groups by intermolecular coordination.

Some preliminary studies were carried out of the reactions of these stannylsulphonamides in comparison with the stannylcarboxamides. The stannylsulphonamides are hydrolysed much less readily in air, and the infrared spectra showed that thin films on sodium chloride plates were hydrolysed only partially in 2 minutes.

Similarly the stannylsulphonamides are less reactive towards multiply bonded reagents. None showed any reaction towards phenyl isocyanate, whereas *N*-(tributylstannyl)-*N*-methylformamide (I, R′ = Me, R″ = H) reacted exothermically to give apparently the adduct (II, R′ = Me, R″ = H), and *N*-(tributylstannyl)acetamide (I, R′ = H, R″ = Me) gave tributyltin isocyanate and acetanilide, perhaps through a similar adduct (eqn. 3); *N*-(tributylstannyl)-*N*-phenylacetamide, however, was inert[5].

$$\underset{\text{(I)}}{Bu_3Sn-NR'-CO-R''} + PhNCO \rightarrow \underset{\text{(II)}}{Bu_3Sn-NPh-CO-NR'-CO-R''} \rightarrow$$

$$Bu_3Sn-NCO + Ph-NR'-CO-Me \qquad (R' = H) \quad (3)$$

The stannylsulphonamides were similarly less reactive than the stannylcarboxamides towards chloral and bromal. The NMR spectra showed that *N*-(tributylstannyl)-*N*-methylformamide (III, R = Bu, R′ = Me, R″ = H), *N*-(triethylstannyl)-*N*-phenylformamide (III, R = Et, R′ = Ph, R″ = H), and *N*-(tributylstannyl)acetamide (III, R = Bu, R′ = H, R″ = Me) reacted rapidly with bromal, and *N*-(tributylstannyl)-*N*-methylformamide [but not *N*-(tributylstannyl)-*N*-phenylacetamide (III, R = Bu, R′ = Ph, R″ = Me)] with chloral, according to eqn. (4).

$$\underset{\text{(III)}}{R_3Sn-NR'-CO-R''} + O{=}CH-CX_3 \rightarrow R_3Sn-O-CH(CX_3)-NR'-CO-R'' \quad (4)$$

(X = Br or Cl)

The stannylsulphonamides reacted incompletely and relatively slowly with chloral, according to eqn. (5). An excess of chloral (*ca.* 1.2 mol.) was added to the

$$Bu_3Sn{-}NR'{-}SO_2{-}R'' + O{=}CH{-}CCl_3 \rightleftarrows Bu_3Sn{-}O{-}CH(CCl_3){-}NR'{-}SO_2{-}R'' \quad (5)$$

stannylsulphonamide in carbon tetrachloride, and the reaction at 55° was followed by the NMR signal of the aldehydic proton which shifted upfield in the adduct. The results were as follows: [compound; % adduct at equilibrium; time to equilibrium; τ(CH) in adduct] 1, 10, 12 h, 3.72; 2, 0, –, –; 3, 0, –, –; 4, 80, 4 days, 4.16; 5, 50, 3 days, 4.12; 6, 50, 24 h, 4.15; 7, 100, 14 h, 4.82 (doublet, J 9.6 Hz).

In both substitution and addition reactions, relative reactivities therefore appear to follow the sequence $R_3Sn{-}NR'_2 > R_3Sn{-}NR'{-}CO{-}R'' > R_3Sn{-}NR'{-}SO_2{-}NR''_2$, consonant with the suggestion (see *e.g.* ref. 6) that the nucleophilic power of the electronegative group of the addendum dominates the reactivity.

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