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Preliminary communication

Sulphinylaminotin compounds

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SUMMARY

The metathetical exchange reaction between tin alkoxides and aminosilanes has been used to prepare the first sulphinylaminotin compounds, which will sulphinylate chlorosilanes, giving notably bis(sulphinylamino)dimethylsilane.

Sulphinylamine derivatives of organic amines[1] and hydrazines[2] have been known since the last century. However, it was not until 1966 that the first sulphinylamine of other Group IV elements was prepared[3]. This involved the reaction of thionyl chloride and tris(trimethylsilyl)amine. Four years later, a method involving the formation of disulphides was successfully applied to sulphinylaminotrimethylgermane[4].

$$(Me_3Si)_3N + SOCl_2 \xrightarrow{AlCl_3} 2Me_3SiCl + Me_3SiNSO$$

$$Me_3MSPh + PhSNSO \rightarrow Ph_2S_2 + Me_3MNSO \ (M = Si, Ge)$$

To date, no sulphinylaminotin compounds have been reported, and bis(sulphinylamino)-sulphide, $S(NSO)_2$, is the only compound known with two of the functional groups on the one atom[5]. This note reports the preparation of sulphinylaminotin compounds and bis(sulphinylamino)dimethylsilane.

The facile exchange between aminosilanes and tri-n-butyltin methoxide gives tin amines in high yield. This exothermic reaction has been successfully applied to the synthesis of sulphinylaminotri-n-butyltin, using the sulphinylaminosilane mentioned above. The product is a high boiling, pale yellow liquid with two peaks in its infrared spectrum at 1260 and 1090 cm^{-1} characteristic of the sulphinylamino group.

$$\text{n-Bu}_3\text{SnOMe} \begin{cases} \xrightarrow{\text{Me}_3\text{SiNMe}_2} \text{n-Bu}_3\text{SnNMe}_2 + \text{Me}_3\text{SiOMe} \\ \xrightarrow{\text{Me}_3\text{SiNSO}} \text{Me}_3\text{SiOMe} + \text{n-Bu}_3\text{SnNSO} \end{cases}$$

Good yields of sulphinylaminotrimethyltin result using trimethyltin ethoxide. Like the n-butyl homologue it is a pale yellow liquid, boiling at 62°/10 mm with n_D^{25} 1.5141 and a single peak in the PMR spectrum centred at τ 9.63 with $J(^{117}\text{Sn–C–H})$ and $J(^{119}\text{Sn–C–H})$ 60.0 and 62.7 cps. Sulphinylaminotrimethylgermane can be prepared by the same method, but the reaction requires the use of aluminium chloride as a catalyst.

$$\text{Me}_3\text{GeOMe} + \text{Me}_3\text{SiNSO} \xrightarrow{\text{AlCl}_3} \text{Me}_3\text{SiOMe} + \text{Me}_3\text{GeNSO}$$

Lappert[6] has reported that dimethylaminotrimethyltin will aminate various covalent fluorides and chlorides, notably chlorotrimethylsilane. Dimethylaminotri-n-butyltin behaves likewise with this and dichlorodimethylsilane, to give the corresponding aminosilanes. With sulphinylaminotri-n-butyltin and these chlorides, good yields of both sulphinylaminotrimethylsilane and the bis(sulphinylamino)silane $\text{Me}_2\text{Si(NSO)}_2$ result.

$$\text{n-Bu}_3\text{SnNSO} \begin{cases} \longrightarrow \text{Me}_2\text{Si(NSO)}_2 + 2\ \text{n-Bu}_3\text{SnCl} \\ \longrightarrow \text{Me}_3\text{SiNSO} + \text{n-Bu}_3\text{SnCl} \end{cases}$$

The latter is a bright yellow liquid with a sweet sickly smell. It shows a single peak in the PMR spectrum at τ 9.38, while intense infrared absorptions at around 1300 and 1100 cm^{-1} support the presence of the sulphinylamino groups, and boils at 54°/7 mm, n_D^{25} 1.4787.

EXPERIMENTAL

While all reactions were conducted in a moisture free atmosphere, those involving the tin compounds involved the exclusion of CO_2 as well. All the reactions were clean, giving yields of the products in excess of 65%.

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