Organotin chemistry

VI*. The stability of unsymmetrically substituted triorganotin oxides**

In spite of the fact that reference to over twenty-five unsymmetrically substituted triorganotin hydroxides*** can be found in the literature, only two members of this class have been isolated and characterized. Kipping[2] reported the preparation of the two hydroxides: phenyl-*p*-tolylbenzyltin hydroxide and phenylbenzylbutyltin hydroxide. Bullard and Vingee[3] reported the isolation of dimethylethyltin hydroxide from the air-oxidation of dimethylethyltin hydride or the caustic hydrolysis of the bromide. The material was characterized only by a tin analysis and described as hygroscopic white needles: no physical properties were reported.

The remaining literature references[4-8] to this class all deal with compounds of structure $R_2R'SnOH$, and, in every case, the hydroxide was formed by the caustic hydrolysis of a halide and, without any purification or characterization, converted directly to an acetate. In many cases the hydroxides are not even mentioned explicitly.

We had occasion to prepare dibutylvinyltin hydroxide[6]. When an etherial solution of dibutylvinyltin chloride was treated with excess aqueous sodium hydroxide a cloudy reaction mixture was obtained. When the phases were split and the ether evaporated the liquid residue was also cloudy. This was filtered again to a clear liquid. Overnight, at room temperature, this liquid again developed cloudiness. Filtration alternated with settling until a stable, clear liquid was obtained in 79 % yield which was identified as dibutyldivinyltin. The solid, from the various filtrations were combined, washed with acetone, and dried. It was identified as dibutyltin oxide. The sequence of reactions involved is

$$2(n\text{-}C_4H_9)_2(CH_2{=}CH)SnCl \xrightarrow{OH^-} 2(n\text{-}C_4H_9)_2(CH_2{=}CH)SnOH \longrightarrow$$

$$(n\text{-}C_4H_9)_2SnO + (n\text{-}C_4H_9)_2Sn(CH{=}CH_2)_2 + H_2O$$

The liquid which deposited dibutyltin oxide is obviously the unstable dibutylvinyltin hydroxide.

The fact that the hydroxide is less stable than the halide from which it derives is not surprising if one views the redistribution reaction as an equilibrium process which is driven to completion by the removal of the insoluble diorganotin oxide, as it is formed. The rapidity of the redistribution of dibutylvinyltin hydroxide under ambient conditions, however, is surprising. For comparison, trimethyltin hydroxide[9] redistributes at 100° C to dimethyltin oxide and tetramethyltin over three days and triphenyltin hydroxide[10] or bis(triphenyltin) oxide[11] redistributes to tetraphenyltin and diphenyltin oxide in refluxing xylene (139°) for two days. These considerations should caution anyone working in this field.

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[*] For paper V of this series, see ref. 1.

[**] Presented at the 145th National Meeting of the American Chemical Society, New York City, September, 1963.

[***] It is impossible to decide, based on the almost non-existent experimental details available, whether the triorganotin hydroxide or the closely related bis-oxide is formed. For this discussion, the terms are used interchangeably, except where otherwise indicated in the text.

Experimental

Attempted preparation of di-n-butylvinyltin hydroxide. A caustic solution of sodium hydroxide (9.0 g, 0.22 mole) in 200 ml of water was added, dropwise, to a clear solution of vinyldibutyltin chloride (59.08 g, 0.20 mole) in 200 ml of ether. A reaction temperature of 30° C was maintained. Fine white solids formed during the caustic addition. The reaction was then stirred for 1 h at room temperature. The phases were separated and the white solids were filtered from each and air dried. The aqueous phase was discarded and the organic phase was dried with anhydrous sodium sulfate. The ether was stripped to a pot temperature of 60° C at 15 mm pressure. The residue was filtered to remove white solids that had formed during stripping. The now clear liquid formed solids upon storage and was filtered clear at various intervals, until no more solids formed. This clear organic liquid weighed 23 g (79 %, 0.08 moles). Its IR spectrum was identical with that of di-*n*-butyldivinyltin. (Found: Sn, 41.09. $C_{12}H_{24}Sn$ calcd.: Sn, 41.36 %.)

The combined white solids, after washing with acetone and drying weighed 10 g (40 %, 0.04 moles). Its IR spectrum was identical with that of di-*n*-butyltin oxide. (Found: Sn, 47.44. $C\,H_{18}OSn$ calcd.: Sn, 47.69 %.)

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Received September 3rd, 1963

J. Organometal. Chem., 1 (1964) 299–300

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J. Organometal. Chem., 1(1963) 97, in Table 2, third column, the last figure (35.12) should read (35.81).