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Preliminary communication

THE 2,2-DIALKYL-1,3,2-DIOXASTANNOLES AND THEIR TELOMERIZATION REACTIONS WITH DIALKYLTIN OXIDES

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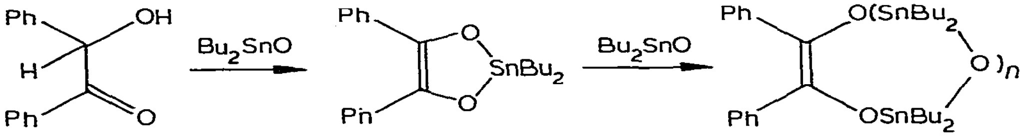
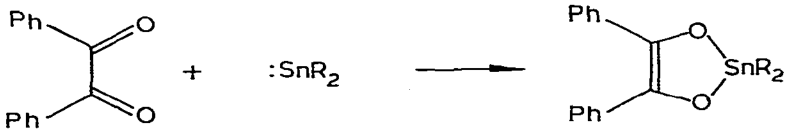
Summary

Benzoin readily reacts with dibutyltin oxide to give the 1,3,2-dioxastannole (A) and thence the dialkylstannoxane oligomers (B) (n = 0—9)



(A) (B)

1,3,2-Dioxastannoles (I) have been reported to be formed when transient (R = Bu) [1] or isolable (R = $Me_2NCH_2CH_2O$) [2] tin(II) compounds react with benzil (eq. 1).



(1)

(I)

We report here a simple new route to the 1,3,2-dioxastannoles, and some of their properties, particularly their telomerization with dialkyltin oxides.

If, for example, dibutyltin oxide and benzoin are heated in benzene under a Dean and Stark water separator, the benzoin behaves as an enediol, and the dialkyltin oxide dissolves in about 1 h to give 2,2-dibutyl-4,5-diphenyl-1,3,2-dioxastannole (II), which is very soluble but can be isolated from pentane at low temperature as an amorphous powder* (see Scheme 1).

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*Satisfactory analyses and IR and NMR spectra have been obtained for all the solid products which are reported.

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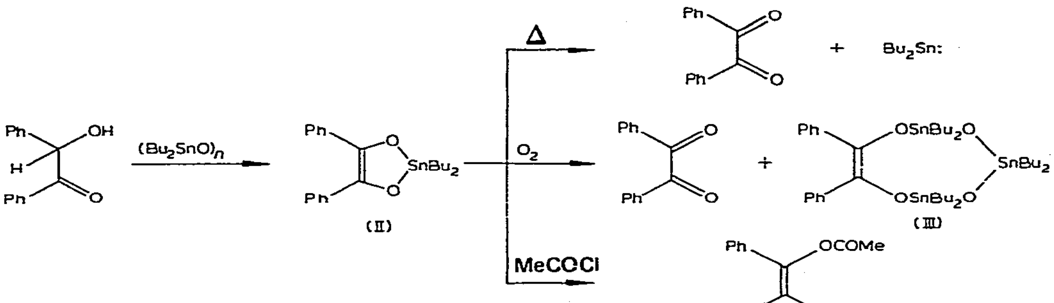
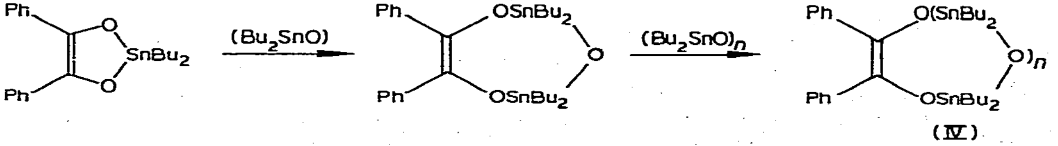


SCHEME 1

If the reaction is carried out in a higher-boiling solvent such as xylene, or if an attempt is made to purify product II by distillation, benzil is formed together with an unidentified organotin residue, suggesting that the dioxastannoles may serve as useful thermal precursors of dialkylstannylenes. Compound II is stable to water, but it is oxidised by air to benzil and the oligostannoxane III (see below).

It is surprisingly unreactive towards heterocumulenes such as isocyanates or isothiocyanates with which the corresponding saturated dioxastannolans react [3], but with acid chlorides or anhydrides (e.g. acetyl chloride) it gives the *cis*-diester in good yield. It seems probable that the dioxastannoles will find applications in organic synthesis similar to those which are being developed for the dioxastannolans [4].

The most remarkable property of the dioxastannoles however is their ability to telomerize with further dialkyltin oxide to cyclic oligomeric dialkylstannoxanes. If benzoin or the dioxastannole II is heated in benzene with the appropriate ratio of dibutyltin oxide, the oxide dissolves to give a clear solution (eq. 2), from which the oligomers (IV; n = 1—9) have been isolated, usually as amorphous powders which turn waxy, and have unsharp melting points, as n increases. The properties of these oligomers, which represent a new class of compounds, are as follows (n, m.p.) 0, 89—90°C; 1, oil; 2, 98—100°C; 3, ca. 140°C; 4, ca. 120°C; 5, ca. 150°C; 9, decomp. The formation of the autooxidation product III can then be rationalized in terms of the initial formation of benzil and of dibutyltin oxides in a highly reactive monomeric or oligomeric form which inserts into the Sn—O bond of the original dioxastannole to give the tristannoxane derivatives (III).



(2)

Acetoin seems to have an almost unlimited capacity to absorb dibutyltin oxide units in this way, to give an oil with an analysis close to that of dibutyltin oxide itself, and such products may find applications as, in effect, a soluble form of the dialkyltin oxides.

The insertion of dialkyltin oxide into an Sn—Cl bond has been demonstrated previously [5] but not into an Sn—O bond. Our preliminary studies suggest that this reaction is not restricted to the unsaturated dioxastannoles, and that it applies also to the saturated dioxastannolans [6].

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