Di-\(n\)-butyldtin Oxide (DBTO)

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Introduction

Di-\(n\)-butyldtin oxide (DBTO), with the composition \(\text{Bu}_2\text{SnO}\), is an amorphous, polymeric powder insoluble in nonreacting solvents. It has been widely used for the selective manipulation of hydroxyl groups and polyols. The largest application of DBTO in organic chemistry is in the generation and reactions of stannylenees from poly-hydroxy compounds. The stannylene acetals may be prepared by refluxing equimolar mixtures of substrate and DBTO in benzene or toluene, with a Dean-Stark apparatus.\(^1\) Recently, Simas has reported that the stannylene intermediate formation does not require removal of water.\(^2\) The synthesis of di-\(n\)-butylstannylene is faster in methanol, but this solvent must be removed prior to addition of the electrophile.\(^3\) Formation of these tin derivatives can be greatly accelerated by microwave irradiation.\(^4\)

Preparation

Di-\(n\)-butyldtin oxide is commercially available from most chemical suppliers. Diorganotin oxides may be obtained by hydrolysis of diorganotin dihalides, diamides, dicarboxylates, or dialkoxides. The hydrolysis is often reversible.\(^5\) Recently, Grossman developed a new procedure: powdered tin metal was reacted with dry \(n\)-butanol at 240 °C for 24 hours; DBTO was formed in 71% yield.\(^6\)

Abstracts

(A) The starting diol was activated by DBTO and then, without isolation of the tin intermediate, treated with an electrophilic reagent\(^2\) (e.g. bromoglycoside,\(^7\) \(\text{BnBr}, \text{allylBr}, \text{BzCl}, \text{TsCl}, \text{or} \, t\)-\(\text{BuMe}_2\text{SiCl}\)), to afford the monosubstituted product. This monosubstitution is regioselective: in most cases only one derivative is isolated.

(B) The original work of David and Thieffry showed that regioselective oxidations of the stannylene by bromine formed an \(\alpha\)- or \(\beta\)-hydroxy ketone.\(^8\) It was later demonstrated that \(N\)-bromosuccinimide (NBS)\(^9\) and \(1,3\)-dibromo-5,5-dimethylhydantoin\(^10\) can replace \(\text{Br}_2\) in this reaction.
(C) Bu₂SnO was used as a catalytic, neutral and mild agent in the preparation of nitriles from the corresponding thioamide or primary alkyl or aryl amides under microwave irradiation or reflux.¹¹

(D) Di-n-butyltin oxide was used to mediate the cycloaddition of trimethylsilyl azide to 4′-methyl-2-biphenylcarbonitrile to give 5-substituted tetrazole in good yield. This tetrazole subunit is important in certain angiotensin II inhibitors.¹²

(E) The dehydrative condensation of 1,2-aminoalcohols with carbon dioxide (5 MPa) has been achieved in N-methylpyrrolidone (NMP) with Bu₂SnO (10 mol%), and 2-oxazolidinones were obtained in 53–94% yield. These are useful intermediates for the synthesis of many target molecules, including polymers, agricultural chemicals, and biologically active compounds.¹³

(F) Diisopropyl L-tartrate was converted to its stannylene acetal and the tin intermediate was directly treated with isothiocyanate. The resulting unstable cyclic N-benzoyliminocarbonate was then immediately treated with a bromide nucleophile (Bu₄NBr). The desired N-benzoyloxazolidin-2-one was obtained in 81% overall yield. This method allows the conversion of syn-diols to syn-amino alcohols.¹⁴

(G) Steliou and Hanessian reported a useful approach towards the preparation of lactones and lactams, including several macrocyclic types (macrolides), directly from α-hydroxy and α-amino carboxylic acids, by using catalytic amounts of DBTO under neutral conditions and without resorting to high dilution techniques.¹⁵

References