

SYNLETT Spotlight 95

Di-*n*-butyltin Oxide (DBTO)

Compiled by Qian Wan



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Qian Wan was born in Wuhan, China in 1975. He received his BSc degree from Central China Normal University in 1997 and began his graduate courses at the same university. In September 1999 he attended the University of Paris-Sud, France, where he completed his 'Diplôme d'Etudes Approfondies' under the supervision of Dr. Claudine Augé in 2000. He is recipient of an Eiffel Scholarship (French Ministry of Foreign Affairs) and is currently working towards his PhD under the supervision of Pr. André Lubineau and Dr. Marie-Christine Scherrmann at the same laboratory. His research interest is in the total synthesis of *C*-disaccharides via a hetero-Diels-Alder reaction and stereo-controlled transformations.

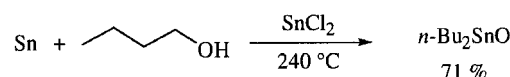
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Introduction

Di-*n*-butyltin oxide (DBTO), with the composition Bu_2SnO , 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 stannylenes from polyhydroxy 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

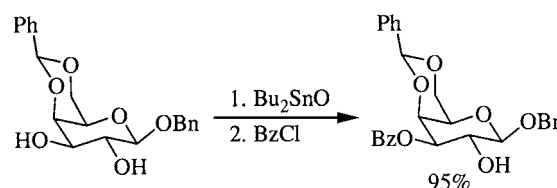
Preparation

Di-*n*-butyltin 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

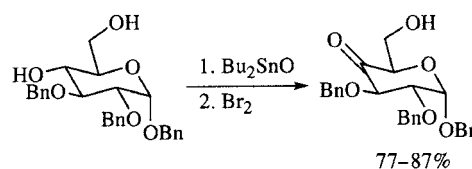


Abstracts

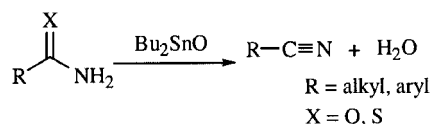
(A) The starting diol was activated by DBTO and then, without isolation of the tin intermediate, treated with an electrophilic reagent² (e.g. bromoglycoside,⁷ BnBr , allylBr, BzCl ,⁸ TsCl , or $t\text{-BuMe}_2\text{SiCl}$), to afford the monosubstituted product. This monosubstitution is regioselective: in most cases only one derivative is isolated.



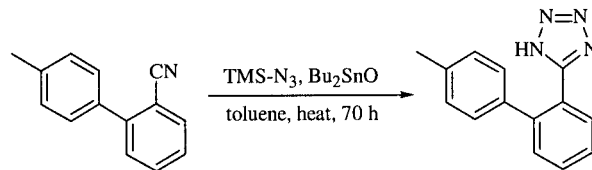
(B) The original work of David and Thieffry showed that regioselective oxidations of the stannylene by bromine formed an α - or β -hydroxy ketone.⁸ It was later demonstrated that *N*-bromosuccinimide (NBS)⁹ and 1,3-dibromo-5,5-dimethylhydantoin¹⁰ can replace Br_2 in this reaction.



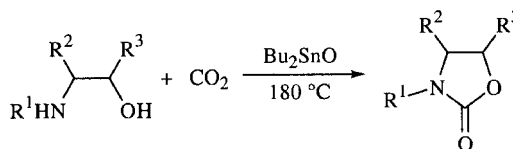
(C) Bu_2SnO was used as a catalytic, neutral and mild agent in the preparation of nitriles from the corresponding thioamide or primary alkyl or aryl amides under microwave irradiation or reflux.¹¹



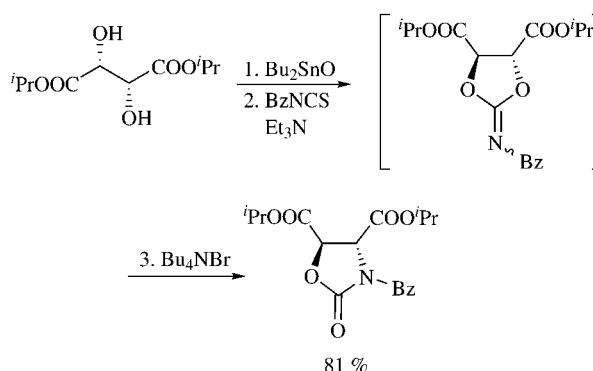
(D) Di-*n*-butyltin oxide was used to mediate the cycloaddition of trimethylsilyl azide to 4'-methyl-2-biphenylcarbonitrile to give 5-substituted tetrazole in good yield. This tetrazole subunit is important in certain angiotensin II inhibitors.¹²



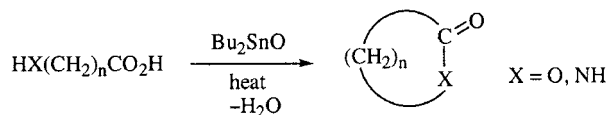
(E) The dehydrative condensation of 1,2-aminoalcohols with carbon dioxide (5 MPa) has been achieved in *N*-methylpyrrolidone (NMP) with Bu_2SnO (10 mol%), and 2-oxazolidinones were obtained in 53–94% yield. These are useful intermediates for the synthesis of many target molecules, including polymers, 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*-benzoyl iminocarbonate was then immediately treated with a bromide nucleophile (Bu_4NBr). 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 ω -hydroxy and ω -amino carboxylic acids, by using catalytic amounts of DBTO under neutral conditions and without resorting to high dilution techniques.¹⁵



References

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