

Oxidative Substitution Reactions of Organotin Compounds with Lead Tetra-acetate

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A new oxidative substitution reaction where an organotin group is replaced by an acetoxy group has been investigated; this reaction has been successfully applied to the synthesis of 4-ylidenebutenolides.

Recently many synthetic methods using organotin compounds have been reported, for example, rearrangement,¹ elimination,² coupling,³ and transmetallation reactions.⁴ Oxidative elimination of the organotin group followed by introduction of an oxygen function into the molecule is a potentially useful method for organic synthesis. However, there are few examples^{5,6} based on this principle and its application is limited.

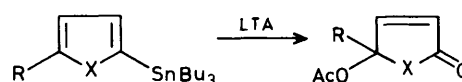
However, using the analogy of silane compounds,⁷ we have assumed that an organotin group would be oxidatively replaced by an acetoxy substituent on treatment with lead tetra-acetate (LTA).

We now describe the results of an investigation into the regioselective oxidative substitution of trialkylstannyl by acetoxy groups. Methylphenoxytri-*n*-butyltin (**1**)⁸ was treated with an equimolar amount of LTA in refluxing dichloromethane under N₂ for 32 h, after which the reaction mixture was poured into water, extracted with dichloromethane, and purified by column chromatography (silica gel) to give methylphenoxyacetate (**2**) and tri-*n*-butyltin acetate in 58% and quantitative yields, respectively.†

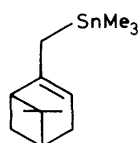
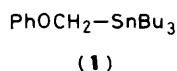
Similarly the stannyl norpinene (**3**)⁹ and cyclohexene (**5**)¹⁰ were treated with LTA to give the corresponding acetates (**4**)

and (**6**) in 55 and 67% yields, respectively. The oxidative substitution occurs regioselectively at the carbon atom attached to tin without oxidation at the double bond.

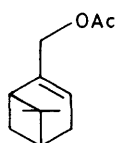
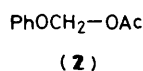
We have applied this oxidative substitution reaction to several heteroaromatic compounds. The tri-*n*-butylstannyl-furans (**7**)–(**10**) and pyrrole (**11**) were synthesized by the reaction of the corresponding 2-lithiofurans or *N*-methyl-2-lithiopyrrole with tri-*n*-butyltin chloride, and the resulting trialkyltin-substituted heterocycles were treated with LTA as described above‡ to give 5-acetoxypyrrole-2(*5H*)-ones (**12**)–(**15**) and 5-acetoxy-1-methyl-3-pyrrolin-2-one (**16**).§



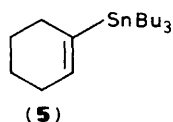
R	X	Yield (%)	Product Yield (%)
H.	O	(7) 87%	(12) 60%
Me.	O	(8) 95	(13) 91
	O	(9) 77	(14) 84
CH ₂ CH ₂ Ph.	O	(10) 72	(15) 55
H.	NMe	(11) 59	(16) 20



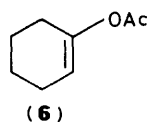
(3)



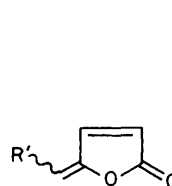
(4)



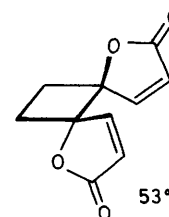
(5)



(6)



(17) R' = H

(19) R' = CH₂Ph; 43%

(18) Anemonin

† Oxidation was also carried out in acetic acid (46 h at 50 °C, 58%) and in benzene (46 h at 50 °C, 8%) as solvents.

‡ An equimolar amount of LTA was used in this reaction. Yield based on LTA. Although a molar ratio of (7): LTA of 1:2 was also used, the yield of butenolides was not improved.

§ It has been reported that 2-furyl acetate was converted to furan-2(*5H*)-one,¹¹ and also 2-siloxyfuran was oxidised with LTA to 5-acetoxypyrrole-2(*5H*)-one.¹² This suggests that the 2-furyl acetate initially formed from the 2-stannylfuran was further oxidised to 5-acetoxypyrrole-2(*5H*)-one.

The acetoxy-substituted furanone (**13**) was heated at 80 °C in acetic acid-acetic anhydride containing a catalytic amount of concentrated sulphuric acid¹³ to give 5-methylenefuran-2(5H)-one (**17**), which immediately dimerised to the natural product anemonin (**18**) (53%), m.p. 158—159 °C (m.p. 158 °C^{13,14}).

Similarly the 4-ylidenebutenolide (**19**) (43%) was synthesized from (**15**). 4-Ylidenebutenolides, which have been frequently found in natural products, display some interesting biological activities,¹⁵ and our method should be applicable to their synthesis.

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