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New Functional Vinyltin Compounds via Diels-Alder Reactions

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New vinyltin reagents are obtained via Diels-Alder reactions, from acetylenic tin derivatives bearing an ester or nitrile group.

[4+2] Cycloadditions are very useful in organic chemistry but have rarely been used to prepare organotin compounds. The tin atom in an acetylenic or ethylenic dienophile has a strong deactivating effect¹ and few examples of these reactions are known.²⁻⁴ With acetylenic compounds this limits us to using hexachlorocyclopentadiene and coumarin as enophiles. However, we thought that Diels-Alder reactions could be achieved if a strongly activating group such as an ester, aldehyde, or nitrile, was incorporated in the starting material to overcome the deactivating effect of tin. By reaction with a diene, vinyl functional tin derivatives, which are valuable intermediates in organic synthesis⁵ could be isolated. Vinylic organotin reagents are usually obtained by addition of tin hydrides,6 tin metal,7 or ditin8 derivatives to acetylenic compounds. These methods are not applicable to six membered rings nor are they regiospecific with carbonyls.9

We first prepared methyl (tributylstannio)propiolate from (dimethylamino)tributyltin and methyl propiolate, equation (1), the known exchange between methoxytributyltin and

$$Bu_{3}SnNMe_{2} + H-C \equiv C-CO_{2}Me \xrightarrow{Et_{2}O, -78 \ ^{\circ}C} Bu_{3}Sn-C \equiv C-CO_{2}Me \qquad (1)$$
(1a)

methyl propiolate giving an impure product. (Tributylstannio)propiolonitrile (**1b**) has been obtained following a known procedure,¹⁰ but we have not been able to obtain (tributylstannio)propiolaldehyde because of a rapid polymerisation of propiolaldehyde in the presence of methoxy- or (dimethylamino)-tributyltin. We showed that the tin precursors undergo smooth [4 + 2] cycloadditions with dienes to give good yields of new cyclic dienic functional organotin reagents, equation (2).

The reactions were performed in sealed Pyrex tubes warmed in a stainless steel autoclave, without solvent and the



Yields of (2a): $R^1 = R^2 = R^3 = H$, 71%; $R^1 = H$, $R^2 = R^3 = Me$, 56%; $R^1 = Me$, $R^2 = R^3 = H$, 66%; (2b): $R^1 = R^2 = R^3 = H$, 74%; $R^1 = H$, $R^2 = R^3 = Me$, 69%.



products were isolated by chromatography on silica gel. With isoprene (yield: 62%) and (1a) a mixture of isomers (1:1) was obtained. With penta-1,3-diene the reaction was highly regiospecific. The product was shown to be greater than 95% of one isomer by ¹¹⁹Sn n.m.r. Protonolysis established that the structure was (2a; $R^1 = Me$, $R^2 = R^3 = H$). Similar results are obtained with methyl propiolate^{11,12} which shows that the presence of the tributyltin moiety does not change the orientation of the cycloaddition. The adduct formed from cyclohexa-1,3-diene and (1a) was not stable and eliminated ethylene to give methyl 2-(tributylstannio)benzoate, equation (3). Adducts (2a) have been easily hydrogenated on Rh/C or aromatised by 2,3,5,6-dichlorodicyanobenzoquinone (DDQ), equation (4).

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