New Functional Vinyltin Compounds *via* Diels–Alder Reactions

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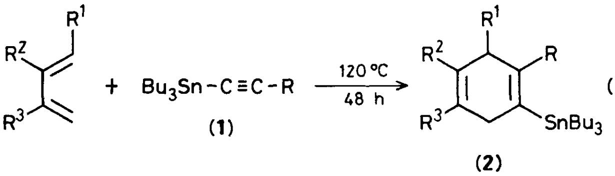
New vinyltin reagents are obtained *via* Diels–Alder reactions, from acetylenic tin derivatives bearing an ester or nitrile group.

[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 effect[1] 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 synthesis[5] could be isolated. Vinylic organotin reagents are usually obtained by addition of tin hydrides,[6] tin metal,[7] or ditin[8] 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 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).

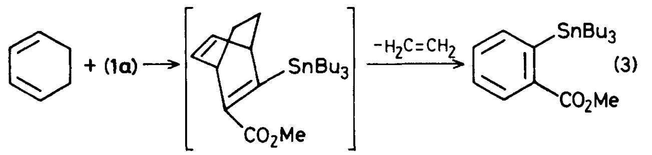
$$\mathrm{Bu_3SnNMe_2 + H{-}C{\equiv}C{-}CO_2Me \xrightarrow{Et_2O,\,-78\,^\circ C} \underset{(\mathbf{1a})}{Bu_3Sn{-}C{\equiv}C{-}CO_2Me}} \qquad (1)$$

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

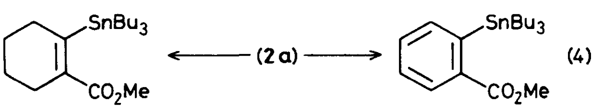


a; R = CO_2Me
b; R = CN

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%.



(3)



(4)

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 ^{119}Sn 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).

Received, 10th July 1984; Com. 989

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