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Preliminary communication

Functionally substituted organotins: formation of organotin-containing phosphines

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Abstract

Additions of P–H bonds to vinylstannes, of Sn–H bonds to alkynylphosphines, and of Sn–P bonds to allenes and alkynes are described.

There are few references in the literature to the functionalisation of organotin compounds by introduction of a phosphine residue. In 1980 Weichmann [1] described the addition of trimethyltin hydride to vinyldiphenylphosphine and of diphenylphosphine to trimethylvinyltin, both reactions yielding the same product:

$$Me_3SnH + H_2C{=}CHPPh_2 \rightarrow Me_3SnCH_2CH_2PPh_2 \leftarrow Me_3SnCH{=}CH_2 + HPPh_2$$

We decided to attempt to extend this work to include substituted vinyl residues and found that only the UV light-catalysed phosphine addition to substituted vinyltins provides a suitable route to compounds $Me_3SnCHRCH_2PPh_2$ ($R = Me$, Ph, Me_3Si, Me_3SN, OEt; yields 75–90%), attempted hydrostannation leading to polymerisation or formation of complex reaction mixtures. The stannyl-substituted phosphines can be readily oxidised by $KMnO_4$ in acetone to give the corresponding phosphine oxides in 61–73% yields.

Alkynyldiphenylphosphines also undergo hydrostannation, e.g.:

$$Me_3SnH + RC{\equiv}CPPh_2 \rightarrow Me_3SnCR{=}CHPPh_2$$

$(R = H, Me_3Sn)$

An alternative approach to organotin-substituted phosphines involves the addition of the Sn–P bond of a stannyl phosphine to a multiple bond. Stannyl phosphines have been known for nearly 30 years [2–8], but have remained somewhat of a laboratory curiosity. Schumann [10] described some reactions carried out with Ph_3SnPPh_2, including its additions to styrene and allyl chloride, and also the addition of Me_3SnPPh_2 to acrylonitrile. Very recently, Stille [11] has reported the palladium-catalysed coupling of Me_3SnPPh_2 and aryl halides to give aryldiphenylphosphines, a reaction that we find to occur under photochemical conditions, although not so cleanly as when the palladium catalyst is present.

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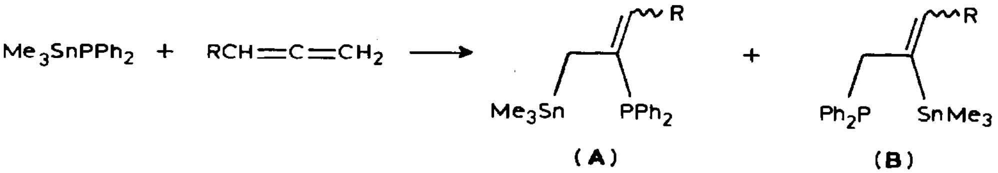
The addition of Me_3SnPPh_2 to alkenes is probably not a particularly useful reaction (styrene polymerises and allyl chloride undergoes substitution), but its addition to both allenes and alkynes under photolytic conditions is much more promising. In the former case a mixture of two regioisomeric products is observed, with that having the phosphine residue attached to the central carbon atom predominating:



The isolated yields and proportions of **A** and **B** are as follows:

R	Yield (%)	A/B ratio
H	78	89/11
Me	67	73/27
Bu	58	88/12
Ph	83	100/0

The last reaction was carried out under thermal conditions (80 °C).

The addition to both terminal and non-terminal alkynes occurs under thermal or photolytic conditions. Schumann [10] reported that Ph_3SnPPh_2 adds to phenylacetylene to give a mixture of the two possible regioisomers, but we find that both this and other terminal alkynes react to give two stereoisomers and that the regiochemistry is uniform:

$$Me_3SnPPh_2 + RC{\equiv}CH \rightarrow (E/Z)\text{-}Me_3SnCH{=}C(R)PPh_2$$

$$(R = Bu, Ph, Et_2NCH_2)$$

Isolated yields are between 60 and 80%: the *E*-isomer is formed preferentially (60–90%). Stannylalkyne and diphenylphosphine are formed as by-products. In the case of non-terminal alkynes, mixtures of (*E*)- and (*Z*)-isomers are again obtained, but regioisomers are absent.

$$Me_3SnPPh_2 + RC{\equiv}CR' \rightarrow (E/Z)\text{-}Me_3SnCR{=}CR'PPh_2$$

$$(R, R' = Ph, Ph;\ Ph, Et;\ MeOCH_2, MeOCH_2)$$

Isolated yields are in this case 50–90%. The (*E*)-isomer is again formed preferentially, but the *E/Z* ratio depends on the reaction conditions used.

All new compounds have been fully characterised by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{119}Sn), structural assignments following from these data.

We are continuing to study these interesting and potentially valuable addition reactions of stannyl phosphines, which appear likely to join the ever-increasing list of important organotin reagents for organic synthesis.

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