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Preliminary communication

DIRECT SYNTHESIS OF ORGANOFUNCTIONAL ARYLSTANNANES

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Summary

Arylstannanes are obtained by direct synthesis from trimethylstannylsodium compounds and the corresponding aryl bromides in 40-78% yield. A reaction mechanism is proposed.

It has long been known that aryltins can be synthesized by the reaction of aryl halides with organostannylalkalis (eq. 1) [1-4]. This reaction is remarkable among nucleophilic aromatic substitutions [5] because it occurs with great facility with unactivated aryl halides. As a part of a systematic study of the

$$R_3SnNa + ArX \rightarrow ArSnR_3 + NaX \quad (1)$$

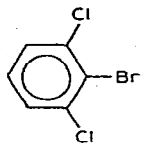
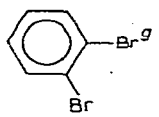
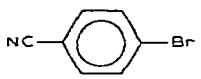
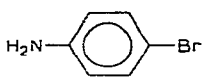
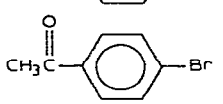
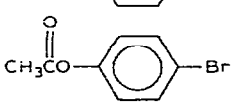
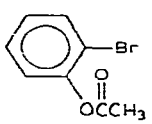
chemistry of organostannyl anionoids we are examining the synthetic scope and mechanism of reaction 1. We report here observations which demonstrate that the reaction has an unexpectedly broad scope as a method for the synthesis of organofunctional arylstannanes.

Reactions were conducted by adding trimethylstannylsodium in tetraglyme (ca. 1 *M*) to an appropriate volume of the aryl bromide (ca. 1 *M*) in the same solvent maintained near 0°C throughout the addition*. The reaction product mixtures were analyzed by GLPC, products were collected and characterized by elemental analyses and PMR spectra. In four cases the reaction products were also treated with water and petroleum ether, the latter layer washed with water, dried over calcium chloride, concentrated, and the product isolated by distillation. Results are gathered in Table 1. The selection shown in the table consists of compounds which could not be prepared by the most important alternative synthesis: reaction of the aryl Grignard reagent with a trimethyltin halide. Attempts to prepare the Grignard reagents from the first two bromides in the table would

*Trimethylstannylsodium was prepared by stirring for 4 h under argon 25 mmol of hexamethylditin with 56 mmol of sodium in 30 ml tetraglyme distilled from sodium. The reaction mixture was filtered through a cotton plug. The yellow-green solution appeared to be stable for many days when stored under a dry inert atmosphere.

TABLE 1

SYNTHESIS OF ORGANOFUNCTIONAL ARYLSTANNANES[a]

ArBr	$ArSnMe_3$ (%)	ArH (%)
	60[b]	—
 [g]	42[b,d,e]	(7)[f]
	80[b]	—
	40[c]	60[c]
	56[c]	43[c]
	78[c]	2[c]
	78[b]	—

[a]Reactions of ArBr with Me_3SnNa in tetraglyme at 0°C. [b]Isolated yield. [c]Yield determined by GLPC. [d]o-Bis(trimethylstannyl)benzene. [e]For an alternate synthesis of o-bis(trimethylstannyl)benzene see ref. 7. [f]Trimethylphenylstannane; percentage determined from area on GLPC trace; not corrected for response factor. [g]o-Dibromobenzene added to trimethylstannylsodium in this case.

result in the formation of benzyne; in each of the other cases the Grignard reagent would react with the functional group attached to the benzene ring.

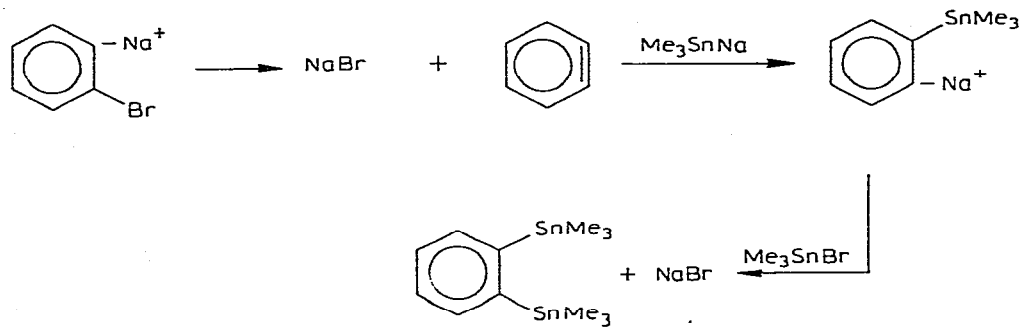
Our mechanistic studies [6] have shown why these syntheses are successful. The most probable mechanism for the substitution is shown in eq. 2. The first

$$R_3SnNa + ArBr \rightarrow ArNa + R_3SnBr \rightarrow ArSnR_3 + NaBr \quad (2)$$

step in the reaction is a nucleophilic substitution by the trimethylstannyl anion on the bromine of the bromobenzene to form arylsodium and trimethyltin bromide. This reaction is much faster than any reaction with the functional groups attached to the benzene rings; in fact, it is faster even than the acid—base reaction with t-butyl alcohol [6]. The arylsodium, in turn, reacts faster with trimethyltin bromide than with the functional groups in most of the examples, as

shown by the yields. The reduction product can be formed by abstraction of a proton by the aryl anion from solvent, carbon α to a carbonyl, or the amino group. Thus, the product distribution depends on the relative rates of nucleophilic displacement on tin and proton abstraction.

In the case of *o*-dibromobenzene one might expect benzyne formation from the *o*-bromophenyl anion. Indeed, when the reaction with this dibromide was carried out in the presence of furan, the Diels—Alder adduct with benzyne was isolated and characterized by PMR, and converted to 1-naphthol by treatment with acid. This suggests eq. 3 as the route to the product in this case. On the other hand, the formation of trimethyl-2,6-dichlorophenylstannane is less likely to involve a benzyne intermediate because it would react as in eq. 3, and 1,2-bis-(trimethylstannyl)chlorobenzene would be expected as a product. The gas chromatogram of the reaction product mixture showed only the isolated reaction product and a small amount of unreacted starting material.



(3)

A limitation of this method of synthesis is indicated by the observation that *p*-bromobenzaldehyde reacted with trimethylstannylsodium to yield only a polymeric product containing no signals from aldehydic hydrogen in the PMR spectrum.

Acknowledgements

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