

Strategies for the synthesis of bi- and triarylic materials starting from commercially available phenols

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Abstract

A series of arylstannanes have been synthesized, through an $S_{RN}1$ mechanism, in good to excellent yields (74–99%) by the photo-stimulated reaction of trimethyl stannyl ion with substrates supporting different nucleofugal groups. The arylstannanes thus obtained were suitable intermediates for Stille cross-coupling reactions leading to asymmetric bi- and triaryl compounds in acceptable global yields. An attractive feature of this route is that simple commercially available benzenediols, chloro- and methoxy phenols might be useful starting substrates, leading the latter to higher global yields of products in fewer steps. The strategies proposed open a broad synthetic tool.

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1. Introduction

Pd-catalyzed cross-coupling reaction has become a very important tool in organic synthesis [1]. Among others, Pd-catalyzed cross-coupling of organotin compounds with carbon electrophiles (the Stille reaction) has been a versatile method for C–C bond formation [2]. In connection with the synthetic importance of these reactions, we are interested in searching new routes to aryl- and vinylstannanes. Thus, application of $S_{RN}1$ reactions [3] to the synthesis of aryl- [4] and vinylstannanes [5] is currently in progress in our laboratory. This alternative route to the synthesis of organostannanes avoids the use of Grignard reagents or organolithium compounds. Recently [4c,4d,4e], we have demonstrated that a triorganostannyl group (Me_3Sn- and Ph_3Sn-) can, with interposition of one additional step, be intro-

duced in place of a phenolic hydroxy group. Specifically, phenols are converted into their diethyl aryl phosphate esters (ArDEP) which on reaction with sodium triorganostannides (Me_3SnNa or Ph_3SnNa) in liquid ammonia afford aryltriorganostannanes by the $S_{RN}1$ mechanism in good to excellent yields (50–100%). It should be noted that, under similar conditions, substrates containing two leaving groups (Cl and DEP) also afford the related disubstitution product in high yield [4d].

Because of their interesting properties, there is a growing interest in the synthesis of valuable bi- and triaryls. Herein we report the synthesis of some trimethylstannyl derivatives and their potential appliance to the construction of mixed bi- and triarylic materials. The organic synthetic strategy proposed is based on the successive selective substitution of suitable leaving groups with trimethyltin anion followed by Pd-catalyzed cross-coupling reactions. An attractive feature of this approach is that simple commercially available derivatives such as benzenediols, chloro- and methoxy phenols might be useful starting substrates.

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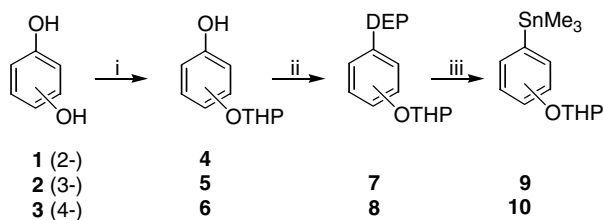
2. Results and discussion

We initiated our investigations employing 1,2-, 1,3- and 1,4-benzenediols as starting materials. The introduction of the first trimethylstannyl group in the aromatic moiety, i.e., the synthesis of the corresponding mono-trimethylstannyl derivatives from these substrates, was carried out as is sketched in **Scheme 1**.

We decided to use tetrahydropyranyl as protecting group taking into account that the hydroxyl group may be easily regenerated under mild conditions. Desymmetrization of benzenediols was carried out with one equivalent of DHP [6a] (step i) affording, in all cases, the desired mono-ether in 30–40% yield, together with starting material (10–30%) and the related di-ether (20–30%). It should be mentioned that each component of the obtained mixtures could be isolated, quantitatively, by column chromatography on silica gel. In the second step (step ii) it was observed that meanwhile the reaction of **5** and **6** with diethyl phosphite led to the corresponding diethyl aryl phosphates **7** and **8** in very good yields (85% and 88%, respectively), the reaction of **4** with diethyl phosphite did not give the desired product (probably because of steric factors) and a complex mixture was obtained. Finally, the photostimulated reaction of **7** and **8** with trimethylstannyl sodium (**11**) (step iii) led, after 4 h, to trimethyl(3-tetrahydro-2*H*-2-pyraniloxyphenyl)stannane (**9**, 84%) and trimethyl(4-tetrahydro-2*H*-2-pyraniloxyphenyl)stannane (**10**, 82%), respectively (**Table 1**, entries 1 and 2). Thus, the mono-stannylated products **9** and **10** were both obtained in 25% overall yield from **2** and **3**. The low yields obtained were essentially owed to the desymmetrization reaction of benzenediols where substantial starting material was lost.

Taking into account that Cl is also a good nucleofugal group in $S_{RN}1$ reactions [4d], we considered of interest to carry out the synthesis of the mono-trimethylstannyl derivatives from commercially available chlorophenols. The route of synthesis is sketched in **Scheme 2**.

In order to compare the yields of these reactions, we used again tetrahydropyranyl as protecting group. The tetrahydropyranyl ethers **14** and **15** were obtained in 90% and 92% yield from **12** to **13**, respectively [6b].



Scheme 1. Reagents and conditions (i) DHP, $AlCl_3$, (ii) $HPO(OEt)_3$, NEt_3 , CCl_4 (iii) Me_3SnNa , $NH_3(liq.)$, $h\nu$.

Table 1
Synthesis of arylstannanes by the photostimulated reaction of ArDEP with **11**

Entry	X ^b	OP ^c	Product and yield (%) ^d
1	DEP	3-OTHP	9 ; 84
2	DEP	4-OTHP	10 ; 82
3	Cl	2-OTHP	16 ; 85
4	Cl	4-OTHP	10 ; 85
5	DEP	4-OMe	21 ; 81 ^e
6	DEP	2-OMe	24 ; 74
7	DEP	3-OMe	25 ; 90

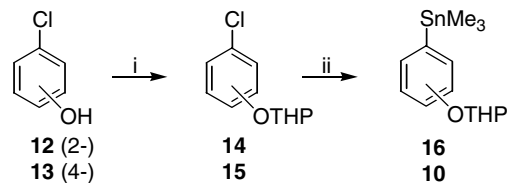
^a Substrate/ Me_3SnNa = 1:1.2.

^b DEP = OP(O)(OEt)₂.

^c THP = tetrahydropyranyl.

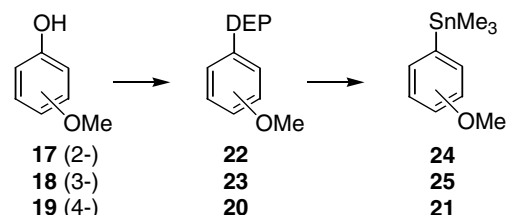
^d Isolated yield of pure products.

^e Ref. [4d].



Scheme 2. Reagents and conditions (i) DHP, p -TsOH. (ii) Me_3SnNa , $NH_3(liq.)$, $h\nu$.

The subsequent photostimulated reaction of **14** and **15** with **11** in liquid ammonia rendered the trimethylstannyl derivatives in excellent yields. Thus, trimethyl(2-tetrahydro-2*H*-2-pyraniloxyphenyl)stannane (**16**) and its isomer **10** were both obtained in 85% yield (**Table 1**, entries 3 and 4). The overall yields of **16** and **10**, from **12** and **13**, were 77% and 78%, respectively; i.e., they were three times higher compared with those obtained from benzenediols. Since the low yields obtained from benzenediols as starting materials were owed to the desymmetrization reaction, we thought that this problem could be solved synthesizing the trimethylstannyl derivatives from commercially available desymmetrized dihydroxyphenols such as 2- (**17**), 3- (**18**) and 4-methoxyphenol (**19**), as is sketched in **Scheme 3**. We have previously proved that the diethyl phosphate ester **20**, derived



Scheme 3.

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