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Preliminary Communication

Palladium-catalyzed coupling reactions of functionalized styryl bromides with 1-propenyltributyltin

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Abstract

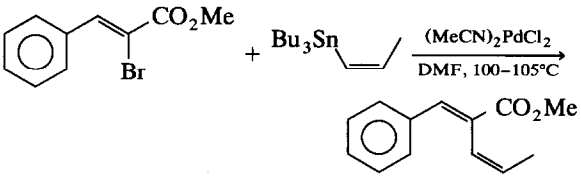
The palladium-catalyzed coupling reaction of 1-propenyltributyltin with functionalized styryl bromides is described. 1,3-Dienes are obtained in low to moderate yields except with β,β-dibromostyrene. The latter undergoes a novel organotin-promoted dehydrobromination-coupling sequence to give a 1,3-enyne as final product.

Key words: Tin; Palladium; Styryl bromide; Coupling reaction; Bromides; Catalysis

The palladium-catalyzed coupling reaction of organotin compounds with organic electrophiles has become an important synthetic method in organic chemistry [1]. This so-called Stille reaction is especially suited for the synthesis of stereodefined 1,3-dienes [2] and 1,3-enynes [3]. Vinylic iodides [3], triflates [4] and mesylates [5] have been commonly used as electrophiles in these reactions, while the more stable and readily available vinylic bromides have been rarely employed [6].

As part of a research program directed towards the synthesis of aromatic 1,3-dienes, we became interested in the Stille reaction. Consequently, a model study of the palladium-catalyzed coupling reaction of functionalized styryl bromides was undertaken, using 1-propenyltributyltin as a representative vinyltin reagent.

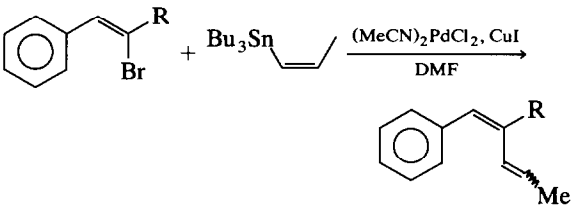
Methyl α-bromocinnamate ($\geq 95\%$ *Z*, 5.0 mmol) was treated with 1-propenyltributyltin (86% *Z*, 5.5 mmol) in the presence of *bis*(acetonitrile)dichloro-palladium(II) (7 mol%) using dry dimethylformamide (DMF, 10 mL) as solvent. The reaction mixture was heated (100–105°C) for 4 days. After work-up, the crude product was purified by column chromatography to give (1*E*,3*Z*)-1-phenyl-2-carbomethoxy-1,3-pentadiene in 47% yield (eqn. (1)). The isomeric purity of this product was $\geq 95\%$, as determined by ^{1}H NMR (300



(1)

MHz) spectroscopy. Using copper iodide as co-catalyst [7] (14 mol%), the same reaction could be run at room temperature with similar results. Without catalysts [8], methyl α-bromocinnamate reacted slowly with 1-propenyltributyltin: after heating at 100–105°C for 4 days, minor amounts of the desired product could be isolated, and, after a week at room temperature, only traces of product could be detected by analytical TLC.

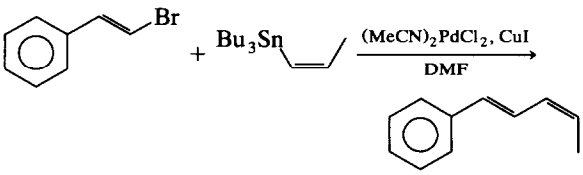
(*Z*)-α-Bromocinnamaldehyde and (*Z*)-α-bromocinnamyl alcohol gave disappointing results when reacted with 1-propenyltributyltin. The first one decomposed at room temperature under the reaction conditions and only about 2% of the corresponding diene could be isolated. The alcohol, in turn, exhibited very low reactivity. At room temperature, no reaction was observed after 4 days. However, heating at *ca.* 100°C in DMF or refluxing in toluene brought about a 19–21% of coupling product as a mixture of isomers (eqn. (2)).



(2)

R = CHO, CH_2OH

β-Bromostyrene (81% *E*) was also treated with 1-propenyltributyltin, according to eqn. (3). After 3 h at *ca.* 100°C, a 85:15 *E,Z*:*E,E* mixture of 1-phenyl-1,3-pentadiene in 30% yield was obtained. By conducting the reaction at room temperature, the conjugated diene could be isolated in 39% yield after 4 days. Minor amounts of homocoupling product, 1,4-diphenyl-1,3-butadiene, were also isolated.



(3)

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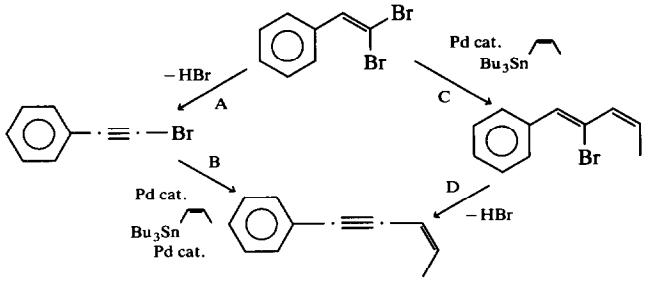
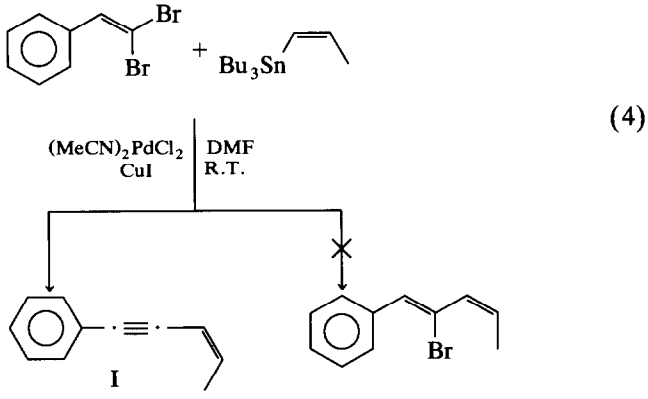


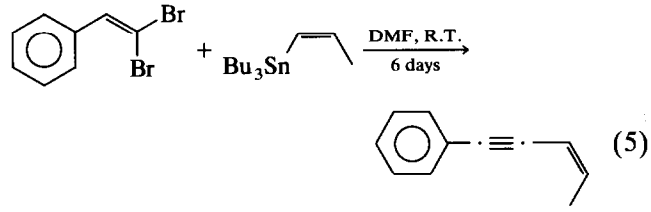
Scheme 1.

In order to obtain information about its stereochemical aspect, we decided to study the coupling process using an 1,1-dibromoalkene. Thus, the reaction of β,β-dibromostyrene with the propenyltin reagent was examined. Surprisingly, the expected 1-phenyl-2-bromo-1,3-butadiene was not produced. Instead, a 26:74 *E*:*Z* mixture of enyne **I** was obtained in 39% yield! (eqn. (4)). To explain the formation of the unexpected product **I**, two possible



(4)

pathways immediately come to mind (Scheme 1): first, the dibromoolefin could undergo a dehydrobromination reaction to give ω-bromophenylacetylene, which, in turn, reacts with 1-propenyltributyltin to produce the enyne **I** (route A–B), or, second, the initially formed 1-phenyl-2-bromo-1,3-butadiene looses HBr under the reaction conditions to give the final product **I** (route C–D). To test the latter possibility, an authentic sample of 1-phenyl-2-bromo-1,3-butadiene was independently synthesized and, subsequently, exposed to the reaction conditions. Careful monitoring of the reaction mixture by analytical TLC showed no evidence for the formation of compound **I**. On the other hand, enyne **I** was produced in 67% yield when ω-bromophenylacetylene was treated with 1-propenyltributyltin under palladium catalysis for 30 min. Furthermore, even in the absence of catalyst [8], 41% of compound **I** was isolated after 5 days. In both reactions, the isomeric composition of enyne **I** was the same obtained in eqn. (4). These results implied that β,β-dibromostyrene is transformed into ω-bromophenylacetylene under the reaction conditions. Control experiments showed that this dehydrobromination reaction was not promoted by the palladium catalyst but rather by the organotin reagent. Indeed, reaction of β,β-dibromostyrene with 1-propenyltributyltin *without catalyst* [8] afforded directly enyne **I** in 25% yield (eqn. (5)).



(5)

I

The dehydrohalogenation of 1,1-dibromoolefins has been reported using alkyllithium reagents or lithium amalgam [9], and as a secondary reaction in the attempted coupling of vinylic dibromides using complex reducing agents [10]. Also, the palladium catalyzed crosscoupling of an organostannane with an iodoalkyne has been recently described [7]. However, it appears that the reaction sequence A–B (Scheme 1) represents the first examples of two chemical events: (i) a relatively slow organotin-promoted dehydrobromination of a 1,1-dibromoalkene, and (ii) a cross-coupling reaction between an alkynyl bromide and a vinyltin compound, which can occur even without palladium catalysis [8]. The mechanism and the synthetic scope of these reactions are presently under investigation and will be reported in future publications.

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