

The Oxidation of Alkoxytributylstannanes with Copper(II) Bromide

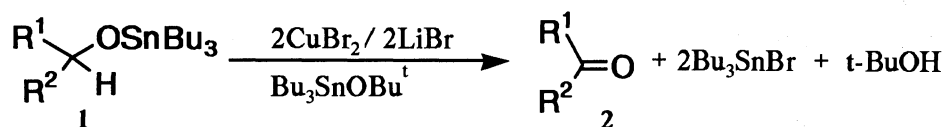
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The oxidation of alkoxytributylstannanes with copper(II) bromide in the presence of lithium bromide and *t*-butoxytributylstannane gave the corresponding carbonyl compounds in good yields under mild reaction conditions.

The oxidation of organic compounds, one of the most basic transformations in organic chemistry, has been widely investigated. Especially, the variety of oxidizing agents have been developed for the oxidation of alcohols to the corresponding carbonyl compounds.¹⁾ However, new chemoselective methods for the oxidation of alcohols under mild conditions are still required in the field of natural product synthesis.

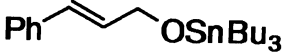
Recently, we showed that allyltributylstannanes were easily oxidized with copper(II) bromide in the presence of the various nucleophilic reagents to give the corresponding coupling products.²⁾ These results indicate that allyltributylstannanes can be used as carbocation species as well as carbanion equivalents according to the substrate and reaction conditions employed. We expected that the copper(II) bromide oxidation could be applied to the oxidation of the various organotin compounds containing hetero-tin bonds. Now, we wish to report the oxidation of alkoxytributylstannanes (1) with copper(II) bromide which affords the corresponding carbonyl compounds under mild conditions as illustrated in the following equation. Concerning the transformation of 1 to carbonyl compounds, Mukaiyama *et al.* reported that bromine is an effective oxidizing agent.³⁾ The similar reaction using *N*-bromosuccinimide (NBS) was also reported.⁴⁾



The starting materials, alkoxytributylstannanes (1), were prepared by the refluxing of alcohols with bis-(tributylstannyl) oxide in toluene with continuous separation of water as the azeotrope.⁵⁾ Initially, we examined the treatment of tributylcinnamyloxystannane (1a) with copper(II) bromide in THF (Table 1). However, almost no reaction was observed (run 1). After several attempts, it was found that the oxidation proceeded to give cinnamaldehyde by the use of lithium salt as an additive (runs 3 and 4). In the oxidation of 1 with bromine, triethylmethoxystannane was found to be an efficient acid capture.³⁾ Similarly, the addition of *t*-butoxytributylstannane suppressed the decomposition of 1a and increased the yield of cinnamaldehyde remarkably (runs 6 and 7).

In a similar manner, the oxidation of various alkoxytributylstannanes was performed. The results listed in Table 2 show that the present oxidation is chemoselective; secondary, allylic, and benzylic alkoxytributylstannanes are

Table 1. Effect of the Additives on the Oxidation of Tributylcinnamyloxystannane (1a)^{a)}

Run	1	Additive equiv.	Time h	Yield %
1		none	18.5	trace
2		LiCl (2.0)	20	—
3		LiBr (2.0)	18.5	31
4	 1a	LiI (2.0)	20	14
5		LiBr (2.0) ^{b)}	20	39
6		LiBr (2.0) ^{c)}	15	56
7		LiBr (2.0) ^{d)}	13	78

a) All reactions were performed with a similar procedure as described in the text, unless otherwise noted.

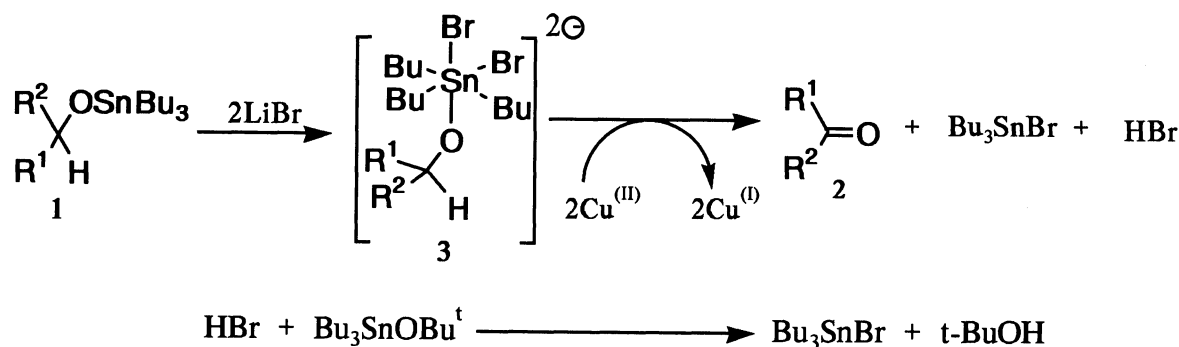
b) 2.0 equivalents of tributylmethoxystannane were used. c) 1.0 equivalent of t-butoxytributylstannane was used. d) 3.0 equivalents of t-butoxytributylstannane were used.

oxidized to the corresponding carbonyl compounds, whereas a simple primary alkoxytinane is unsusceptible to copper(II) bromide (see run 12). The direct oxidation of alcohols without isolation of the alkoxytinanes (1) was also examined. Alcohols were treated with sodium hydride and tributyltin chloride successively in THF⁶⁾ and then oxidized with copper(II) bromide. It was found that the comparable yields of alcohols were obtained by these reactions (runs 2, 7, and 10).

The typical experimental procedure is as follows: To a THF (3 ml) solution of lithium bromide (96 mg, 1.1 mmol) and copper(II) bromide (335 mg, 1.5 mmol) was added t-butoxytributylstannane (0.46 ml, 1.5 mmol) and a THF stock solution of tributyl(1,2,3,4-tetrahydro-1-naphthoxy)stannane (1h) (2.57 ml, 0.5 mmol) at room temperature under argon atmosphere. After 12 h, the reaction mixture was quenched by addition of 10% potassium fluoride solution. The resulting precipitate was filtrated off and the organic material was extracted with CH₂Cl₂. The extract was washed with 10% sodium hydroxide solution, dried over Na₂SO₄, and condensed under reduced pressure. The residue was chromatographed on silica gel (hexane : AcOEt = 9:1) and then 3,4-dihydro-1(2H)-naphthalenone (65 mg) was obtained in 89% yield.

It has been suggested that the oxidation of alkoxytributylstannane (1) with bromine or NBS proceeds through six-membered cyclic transition state.^{3,4)} Considering the fact that copper(II) salt promotes one-electron oxidation, it is not reasonable to assume that the present reaction proceeds such a transition state.

In the following scheme, the hypothetical reaction path way is outlined. As noted earlier, lithium salt is



indispensable to the present reaction. This fact strongly suggests the formation of six-coordinated tin(IV) compound (3) in the reaction. Although the details of the oxidation process is uncertain at present, the carbonyl compounds (2) are produced by the oxidation of the six-coordinated anion (3) with copper(II) bromide. Hydrogen bromide, which decomposes the alkoxytinnane (1), is immediately captured by t-butoxytributylstannane.

It should be noted that the present reaction is the first one in which copper(II) salt is employed for the oxidation of alcohols to carbonyl compounds. Further study including the investigation of the reaction pathway is now in progress.

References

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- 6) The experimental procedure is as follows: To a THF (2 ml) suspension of sodium hydride (55% dispersion in mineral oil; 36 mg, 0.83 mmol) was added a THF (1 ml) solution of alcohol (0.5 mmol) at room temperature. After 30 min, tributyltin chloride (0.15 ml, 0.55 mmol) was added to the reaction mixture, and the mixture was stirred for 1.5 h.

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