

Efficient allylation of aldehydes with allyltributylstannane catalyzed by CuI

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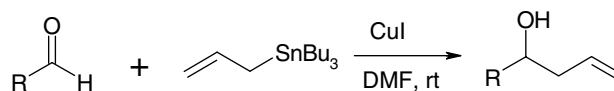
Abstract—Cuprous iodide has been found to be a very effective catalyst for allylation of aldehydes with allyltributylstannane. The catalytic system efficiently promotes the allylation reaction in DMF to produce homoallylic alcohols in high yield.

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The addition of allyl metal reagents to aldehydes is an important method for carbon–carbon bond formation.¹ The utility of this method has been demonstrated by numerous applications in organic synthesis.¹ In recent years, several Lewis acids, especially metal Lewis acids, or transition metal complexes have been utilized extensively to catalyze this transformation.^{2–11} However, methods using Lewis acids must be carried out under strictly anhydrous conditions. Although rhenium complex⁹ and scandium triflate¹⁰ are very effective as air-stable and water-tolerant catalysts for allylation reaction, they are very expensive. Moreover, the rhenium complex catalyses allylation reactions only at high temperatures.⁹ Recently, cerium(III) chloride (CeCl₃·7H₂O) in combination with NaI has been used as a stoichiometric promoter for the allylation of various aldehydes with allyltributyltin.¹² The major drawback of this method is the use of a stoichiometric amount of the promoter to effect the reaction. Several Pd-complexes have also been used as catalysts to carry out this transformation,¹³ however, palladium compounds are expensive. In some cases, toxic metals such as selenium have been used to prepare catalysts.^{13c} The use of silver triflate for allylation reactions has also been reported by many researchers,¹⁴ but silver triflate is expensive and the method requires stringent dry reaction conditions at low temperature. Very recently, Zhao et al. reported a new method for homoallylic alcohol synthesis using a polymer-supported sulfonamide of *N*-glycine as catalyst.¹⁵ This method required a relatively long reaction time to achieve good yields. Moreover, the catalyst is

not available commercially and requires a multi-step procedure for its preparation. There has been increasing interest in the development of new catalysts, which are cheap, air-stable, and easily available commercially. Recently, CuI has emerged as a very effective catalyst for various organic transformations.¹⁶ In this Letter, we report a general and practical method for the synthesis of homoallylic alcohols using CuI as a catalyst (Scheme 1).

Initially, a systematic study on the synthesis of homoallylic alcohols was carried out using benzaldehyde as a substrate. In a typical reaction, allyl tri(*n*-butyl)tin (1 equiv) was added to a mixture of PhCHO and CuI (10 mol % based on PhCHO) in acetonitrile at room temperature. A comparative study was also carried out for evaluation of the catalyst using different solvents such as acetonitrile, dichloromethane, and dimethylformamide (Table 1). The reaction took relatively longer time to occur in acetonitrile, whereas the reaction did not proceed at all in dichloromethane. Dimethylformamide gave the best results. Thereafter, we carried out the experiment varying the amount of catalyst (5–20 mol %). The use of just 15 mol % of CuI was sufficient to drive the reaction to completion in 45 min and in good yield. An increase in the amount of catalyst did not improve the result to any great extent.



Scheme 1.

Keywords: CuI; Allylation; Allyltributylstannane; Aldehyde; Catalyst.

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Table 1. Synthesis of homoallylic alcohols from benzaldehyde under various conditions^a

Entry	CuI (mol %)	Solvent	Time (min)	Yield ^b
1	10	MeCN	120	63
2	10	CH ₂ Cl ₂	720	0
3	10	DMF	60	78
4	5	DMF	90	70
5	15	DMF	45	86
6	20	DMF	35	87

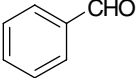
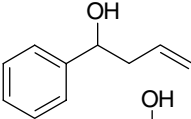
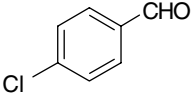
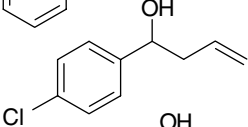
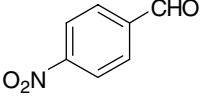
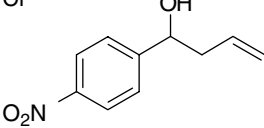
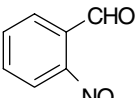
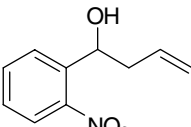
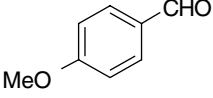
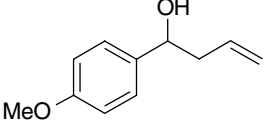
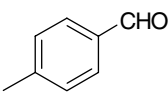
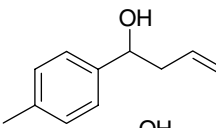
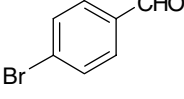
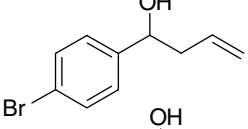
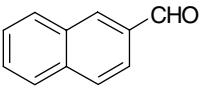
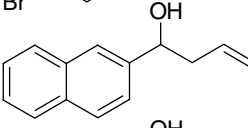
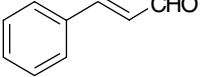
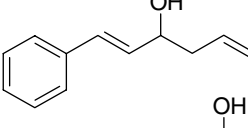

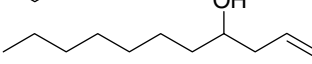
^a Reaction conditions: Benzaldehyde: (1 mmol), allyltributylstannane (1.05 mmol), solvent (2 mL), 25 °C.

^b Isolated yield after chromatographic purification.

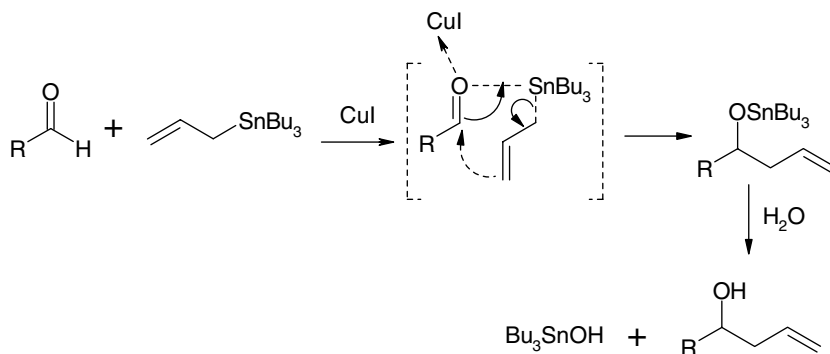
After optimizing the reaction conditions we extended the procedure using different aldehydes, the results are summarized in Table 2. The reaction was carried out

using 1 mmol of aldehyde, and 1.05 mmol of allyltributylstannane, 0.15 mmol of CuI in DMF (2 mL).¹⁷ The reaction mixture was stirred at room temperature for the appropriate amount of time (TLC). Both aromatic and aliphatic aldehydes underwent homoallylation in 69–86% yields. Substituted benzaldehydes such as 4-chloro-, 4-nitro-, 2-nitro-, 4-methoxy-, 4-methyl-, and 4-bromo- were examined under the optimized reaction conditions (entries 2–7). Aldehydes possessing nitro and methoxy groups gave lower yields. The catalyst was quite effective in the case of the sterically congested substrate, 2-nitrobenzaldehyde, giving the product in 69% yield (entry 4). Under similar conditions naphthaldehyde also underwent allylation to the corresponding homoallylic alcohol in 84% yield (entry 8). We extended the procedure to the aliphatic aldehyde, octanal, and an aldehyde containing a double bond, viz. cinnamaldehyde.

Table 2. Synthesis of homoallylic alcohols using the CuI/DMF system

Entry	Aldehyde	Time (min)	Product	Yield ^a
1		45		86
2		45		86
3		75		75
4		50		69
5		120		72
6		60		82
7		50		81
8		60		84
9		90		72
10		60		79

^a Isolated yield after chromatographic purification.



Scheme 2. Probable mechanistic pathway.

hyde. High yields of the respective homoallylic alcohols were obtained under the same catalytic reaction conditions (entries 9 and 10).

A probable mechanistic pathway to explain the homoallylation process is depicted in **Scheme 2**. The reaction may proceed by initial coordination of CuI with the carbonyl compound which facilitates O–Sn bond formation. Subsequent hydrolysis of OSnBu₃ yielded the homoallylic alcohol.

In conclusion, we have developed an efficient protocol for the allylation of aldehydes with allyltributylstannane using CuI as a catalyst. This method has wide scope for further applications as the catalyst is cheap and easily available commercially.

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- Typical procedure:* To a mixture of aldehyde (1 mmol) and CuI (0.1 mmol) in DMF (2 mL), allyltributylstannane (1.05 mmol) was added and the reaction was stirred for the appropriate amount of time (TLC). After completion of the reaction, ether (10 mL) was added followed by addition of water (5 mL). The mixture was stirred for 10 min and the ethereal layer was separated. The aqueous layer was extracted twice with 10 mL portions of ether. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. Ether was evaporated and the crude product was purified by column chromatography over silica gel (230–400 mesh) using petroleum ether–ethyl acetate mixture as eluent.