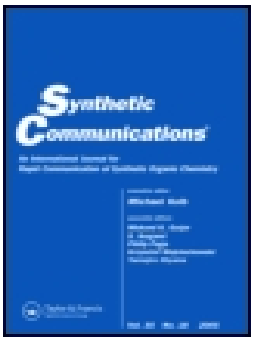

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Efficient Synthesis of Homoallylic Alcohols/Amines from Allyltributylstannane and Carbonyl Compounds/Imines Using Iodine as Catalyst Under Acetic Acid–Water Medium

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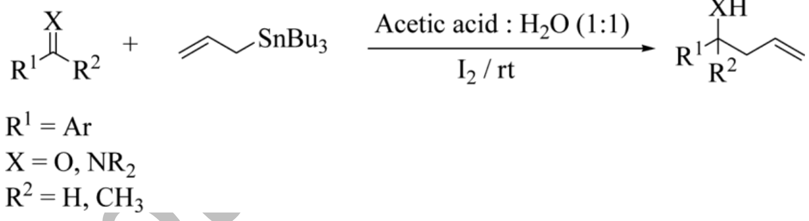
Abstract

This paper describes a general method for the synthesis of homoallylic alcohols and amines by nucleophilic addition reaction of allyltributylstannane to carbonyl compounds and aldimines where iodine acts as a catalyst in H_2O:acetic acid (1:1) medium. Only 10 mol % of I_2 is required for various organic transformations. By using this process, various homoallylic alcohols and amines are produced in good to excellent yield.



KEYWORDS: Allylation, Carbonyl compounds, Aldimines, Iodine

INTRODUCTION

Allylation of carbonyl compounds and aldimines to produce homoallylic alcohols and amines respectively has been widely investigated and established a powerful tool to synthesize valuable intermediates such as β-hydroxy carbonyl compounds, β- and γ-amino acids, spiro cyclic compounds and γ-lactams. They have attracted significant attention due to their versatile uses as important building blocks for natural product synthesis.[1] Hence, numerous reagents and methods have been developed to accomplish this transformation.[2] A number of methods have been developed for allylation reaction involving various metals[3] such as zinc, tin, indium, bismuth, manganese, magnesium, antimony, scandium, cobalt, cerium and silver. Wolinsky and his co-workers[4] reported the allylation of aldehydes and ketones with allyl bromide mediated by 'activated' zinc dust in 95% ethanol at 78 ^{o}C. Araki *et al.* reported the allylation of carbonyl compounds using indium metal in an anhydrous organic solvent.[5] Later, Li and Chan successfully carried out the indium-mediated, Barbier-type allylation in aqueous medium.[6] Nokami *et al.* [7] observed that water had an accelerating effect on the allylation of carbonyl compounds with diallyltin dibromide in ether. Chen[8] reported Sb-mediated allylation in alcohol-water mixture. Jarvo *et al*.[9] reported silver bromide catalyzed allylation of aldehydes and ketones using unactivated manganese powder. In the same year Wu and Sun[10] reported the facile allylation of N-Boc and N-Cbz imines by using allyltrichlorosilane promoted by DMF and acetonitrile at 0 °C. Wang[11] and his co-workers used tin nano particles for the allylation of aldehydes and ketones in aqueous medium. Slaton *et al.*[12] reported tin mediated Barbier-type allylation in ionic liquids. In the same year, Li and his co-workers[13] reported a mild and efficient allylation reaction mediated by magnesium powder under solvent-free conditions. Guo *et al.*[14] reported a method for the allylation reaction of the carbonyl compounds using 2 molar eqiv. of Cu powder to accomplish the product formation. Bellucci *et al.*[15] developed a method for the allylation of imines promoted by lanthanide triflates. One year later, Wang[16] and his co-workers reported that imines can be allylated by magnesium or zinc mediated Barbier-type procedure to produce homoallylamines in excellent yields. Phukan[17] reported that only 10 mol% iodine catalyzes efficiently the three-component reaction of aldehydes, benzyl carbamate and allyltrimethylsilane to afford the corresponding protected homoallylamine in good to excellent yield. Yadav *et al.*[18] reported the allylation and alkynylation of cyclic allylic acetates with allyltrimethylsilane and alkynyl silanes in the presence of molecular iodine in dichloromethane at rt. Although a number of allylating reagents are used for the allylation reaction, allyltributylstannane is one of the most common reagents used for the synthesis of homoallylic alcohols and amines. Generally, strong Lewis acids such as $TiCl_4$ and $BF_{3.\,O}Et_2$ and other metal complexes such as $PdCl_2(PPh_3)_2$, $PtCl_2(PPh_3)_2$, bis-π-allyl palladium complex, lanthanide salts and $LiClO_4$ are used for the preparation of homoallylic amines.[19] However, in most of allylation reactions of carbonyl compound, either low yield[12, 14] or prolonged reaction time[9] is needed. Also, metal triflates are highly expansive.[15] Therefore, the development of novel, common, cheap, high yielding and useful catalytic methods is of interest. Iodine has emerged as a very effective catalyst for various organic transformations.[20] In continuation of our work on various allylation reaction,[21] we wish to report herein a method for the synthesis of hommoallylic alcohols and amines by nucleophilic addition reaction of allyltributylstannane to carbonyl compounds and aldimines using I_2 as catalyst in the presence H_2O:acetic acid (1:1) (Scheme 1).

RESULTS AND DISCUSSION

In a typical reaction, aldehydes (1 mmol), allyltributylstannane (1 mmol) and I_2 (5 mol %) were added successively in H_2O:acetic acid (1:1; 1 mL) at room temperature. The reaction was monitored by TLC. The results are presented in Table 1. Initial experiment without acetic acid failed to produce any product at room temperature (Table 1, entry 1). Another experiment without both H_2O and the catalyst also produced negative result (Table 1, entry 2 and 3 respectively). When the reaction was examined using iodine as catalyst (5 mol%), in a mixed solvent system H_2O-acetic acid at the ratio of 1:1, it produced 58% of the product formation after 1 h at room temperature (Table 1, entry 4). The reaction with increasing the concentration of the catalyst as well as allyltributylstannane gradually increases the yield of the reaction up-to 95%. However, the reaction showed positive results when we examined the reaction by using some Lewis acid e.g. CuI and $FeCl_3$ as catalyst where the corresponding homoallyl alcohols produced moderate to low yield respectively (Table 1, entry 14 and 15). The reaction was also examined using different solvents such as THF, CH_3CN, DMF, DMSO and CH_2Cl_2 (Table 1, entries 9–13). But, in every cases, the reaction was found to be inactive for product formation. Finally, the use of 10 mol % of I_2, 1.2 equiv of allyltributylstannane and 1 equiv of benzaldehyde in H_2O:acetic acid (1:1; 1 mL), was found to be optimum to realize the best yield of the product.

After establishing the optimized reaction conditions, a variety of aromatic and aliphatic aldehydes were investigated under the same reaction conditions. The results are summarized in Table 2. In general, the procedure works well for a variety of aliphatic as well as aromatic aldehydes to produce the corresponding homoallylalcohols in excellent yield. Substituted aromatics bearing the groups –Cl, -OMe, -Br, $-NO_2$, $-CH_3$ reacted very successfully no matter the substituent position in the aromatic ring produced high yields.

The success of the homoallylation of the aldehydes prompted us to extend the procedure to ketones (Table 2, entry 13-18) and aldimines (Table 3) which were produced in situ of the reaction between aldehydes and amines. Initial experiment with acetophenone produces 76 % yield after 2 h (Table 2, entry 13) of the reaction time. The reaction was further extended to a variety of ketones in which cases both aromatic, cyclic and aliphatic ketones produces excellent yield with slightly longer reaction time.

CONCLUSION

In summary, we have developed a method for allylation reaction of aldehydes, ketones and imines with allyltributylstannane in acetic acid-water medium. The advantages of these methods include the use of a nontoxic catalyst, easy to handle and the generation of homoallyl alcohol and amine in one step. Further investigation regarding the asymmetric version of this reaction in the same solvent system is currently in progress in our laboratory.

EXPERIMENTAL

All the chemicals used were of analytical grade. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ at 300 and 75 MHz respectively, using Bruker Ultrashild 300 MHz spectrometer (TMS as internal reference). Mass spectra were recorded on a Perkin Elmer Clarus 600 C mass spectrometer. IR spectra were recorded by using Perkin Elmer Spectrum RX IFT-IR Spectrometer.

Synthesis Of 1-Phenyl-But-3-En-1-Ol

A mixture of benzaldehyde (106 mg,1 mmol), allyltributylstannane (397 mg, 1.2 mmol) and I_2 (25.3 mg, 0.1 mmol) were added in H_2O:AcOH (1:1, 1 mL), at room temperature. After stirring the reaction for appropriate time (checked by TLC) the solution was added to water and the reaction mixture was extracted with diethylether (3 x 10 mL). The combined organic extract was dried over sodium sulphate, filtered and concentrated. The crude product was purified by flash column chromatography over silica gel (230-400 mesh) using ethylacetate-petroleum ether (5:95) as eluent.

1-Phenyl-but-3-en-1-ol (3a). IR (υ/cm^{-1}): 3372, 3073, 2907, 1641, 1493, 1445, 1043; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.23 (m, 5H), 5.91-5.72 (m, 1H), 5.24-5.11 (m, 2H), 4.80-4.70 (m, 1H), 2.60-2.45 (m, 2H), 2.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 134.4, 128.4, 127.5, 125.8, 118.5, 73.3, 43.8; ESIMS (m/z) 149 $[M+H]^+$.

Benzyl-(1-phenyl-but-3-enyl)-amine (6a). IR (υ/cm^{-1}): 3460, 3058, 2921, 1489; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97-7.01 (m, 9H), 5.80-5.60 (m, 1H), 5.18-4.92 (m, 2H), 4.22-4.10 (m, 1H), 3.46 (d, *J* = 12 Hz, 1H), 3.40 (d, *J* = 12 Hz, 1H), 2.60 (s, 1H, NH), 2.40-2.10 (m, 2H); ESIMS (m/z) 238 $[M+H]^+$.

ACKNOWLEDGEMENTS

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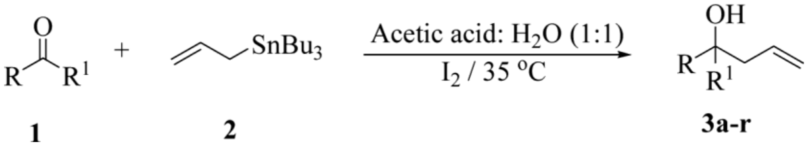
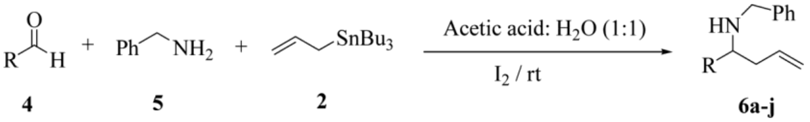
Table 1 Synthesis of homoallylic alcohols from Benzaldehydes using I_2 as a catalyst.

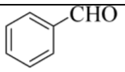
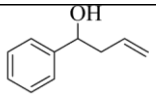
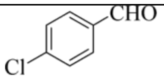
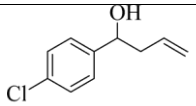
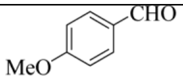
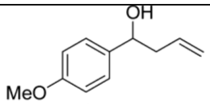
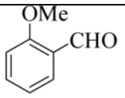
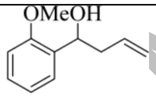
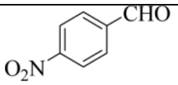
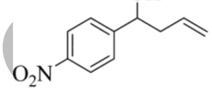
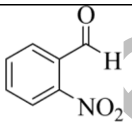
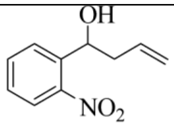
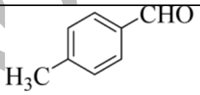
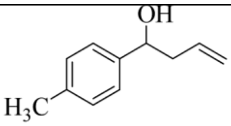
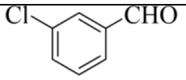
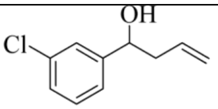


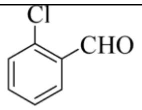
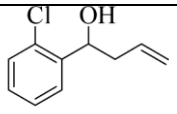
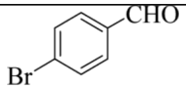
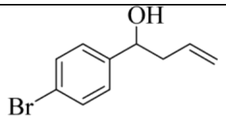
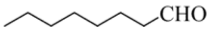
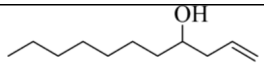
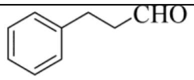
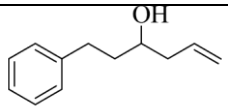
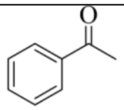
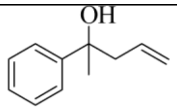
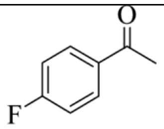
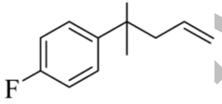
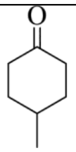
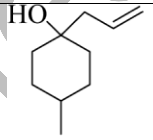
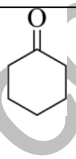
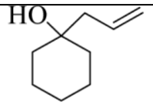
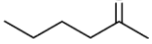
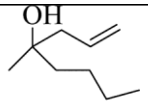
Entry	PhCHO (mmol)	Solvent (mL)	Acetic acid (mL)	Allyl tributylstannane (mmol)	Catalyst (mol%)	Time (h)	Yield[a] (%)
1	1	H_2O (1)	-	1	I_2 (5)	24	0
2	1	-	1	1	I_2 (5)	24	0
3	1	H_2O (1)	1	1	-	24	0
4	1	H_2O (1)	1	1	I_2 (5)	1	58
5	1	H_2O (1)	1	1.1	I_2 (5)	1	82
6	1	H_2O (1)	1	1	I_2 (10)	1	80
7	1	H_2O (1)	1	1.1	I_2 (5)	1	90
8	**1**	H_2O (1)	**1**	**1.2**	I_2 (10)	**1**	**95**
9	1	THF (1)	-	1.2	I_2 (10)	24	0
10	1	CH_3CN (1)	-	1.2	I_2 (10)	24	0
11	1	DMF(1)	-	1.2	I_2 (10)	24	0
12	1	DMSO (1)	-	1.2	I_2 (10)	24	0
13	1	CH_2Cl_2 (1)	-	1.2	I_2 (10)	24	0
14	1	H_2O (1)	1	1.2	CuI (10)	1	40
15	1	H_2O (1)	1	1.2	$FeCl_3$(10)	1	10

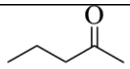
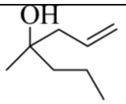
[a] isolated yield after chromatographic purification

Table 2 Acetic acid:H_2O mediated and I_2 catalyzed allylation of aldehydes[a]



Entry	Aldehydes/Ketones	Product[b]	Time(h)	Yield(%)[c]
1		 **3a**	1.0	95
2		 **3b**	1.0	83
3		 **3c**	1.0	88
4		 **3d**	1.0	92
5		 **3e**	1.0	76
6		 **3f**	1.0	87
7		 **3g**	1.0	85
8		 **3h**	1.0	93

9		 **3i**	1.0	88
10		 **3j**	1.0	83
11		 **3k**	2.0	79
12		 **3l**	2.0	82
13		 **3m**	2.0	76
14		 **3n**	2.2	93
15		 **3o**	2.0	83
16		 **3p**	2.5	85
17		 **3q**	2.2	83

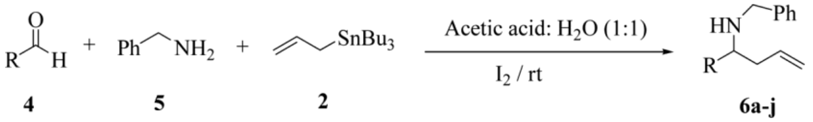
18		 **3r**	2.5	82

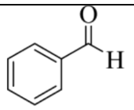
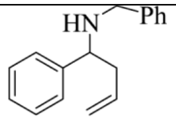
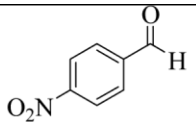
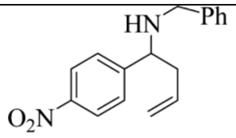
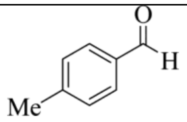
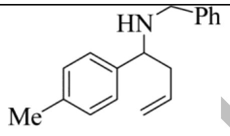
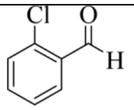
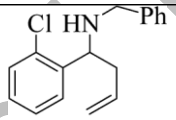
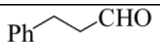
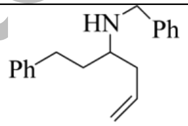
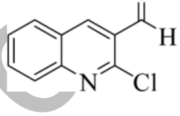
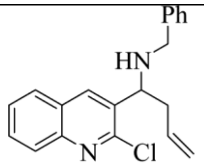
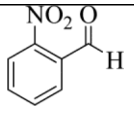
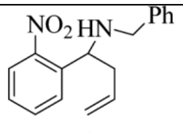
[a]Reaction condition: Aldehydes/Ketones, 1 mmol; Allyltributylstannane, 1.2 mmol; H_2O:AcOH = 1:1; I_2, 10 mol %

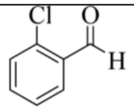
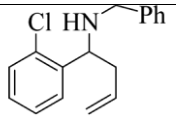
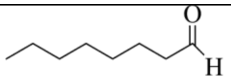
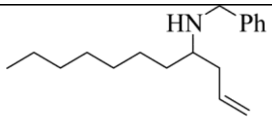
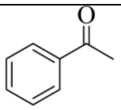
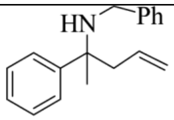
[b]All products were characterized by IR, ^{1}H NMR and ^{13}C NMR.

[c] Isolated yield after chromatographic purification.

Table 3 I_2 catalyzed three-component synthesis of homoallylic amines[a]



Entry	Reactant	Product[b]	Time (h)	Yield (%)[c]
1		 **6a**	2.0	83
2		 **6b**	2.5	92
3		 **6c**	2.0	73
4		 **6d**	2.0	84
5			2.0	77
6		 **6f**	2.5	88
7		 **6g**	2.5	89

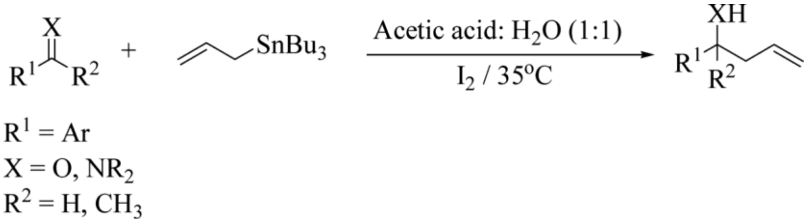
8		 **6h**	2.0	82
9		 **6i**	2.0	81
10		 **6j**	2.5	Trace

[a]Reaction condition: Aldehyde, 1mmol; benzylamine, 1 mmol; allyltributyltin, 1.2 mmol; H_2O:AcOH = 1:1; I_2, 10 mol %.

[b]All products were characterized by IR, ^{1}H NMR and ^{13}C NMR.

[c]Isolated yield after chromatographic purification.

Scheme 1



R^1 = Ar
X = O, NR_2
R^2 = H, CH_3