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Trifluoromethane Sulphonic Acid: a Brönsted Acid Catalyst for the Addition of Allyltributylstannanes to Carbonyl Compounds in Water

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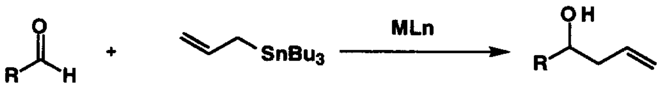
Abstract: Trifluoromethane sulphonic acid catalyses the addition of allyltributylstannane to carbonyl compounds in water to give the corresponding homoallylic alcohols in high yields.

Keywords: Trifluoromethane sulphonic acid; allylation; aldehydes; water

The development of new Lewis acid-catalyzed C-C bond formation reactions in water has been an area of great interest amongst organic chemists[1,2]. Accordingly, much effort has been focused on the development of new water stable Lewis acids, including most recently on the use of indium trichloride as an efficient catalyst for the catalysis of the Mukaiyama aldol reaction in water[3,4,5,6,7]. Our continuing interest in developing new methodologies in water has prompted us to search for new Lewis acid or Brönsted acid-catalyzed C-C bond formation reactions in water. Although the allylation of aldehydes with allytributyltin has been elegantly achieved by using Sn catalysts in acidic aqueous media, the reaction of allytributyltin with carbonyl compounds in the presence of HCl does not afford the allylation product[8]. In this paper, we show that trifluoromethane sulphonic acid (CF_3SO_3H) catalyzes the reaction of allyltributylstannanes[9-23] with carbonyl compounds in water to afford the corresponding products in moderate to good yields.



Scheme 1

Firstly, we studied the effect of a wide variety of Lewis acids and mineral acids on the reactivity of allyltributyltin with benzaldehyde in water. Unfortunately, most of the Lewis acids and mineral acids were not effective in catalyzing the formation of the allylation product and considerably lowered reaction rates and yields were noted. We were

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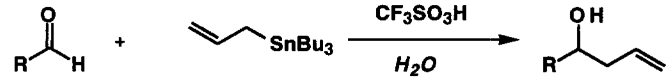
not successful until we chanced upon trifluoromethane sulphonic acid which afforded the desired product in moderate yield (Table 1, entry 4).

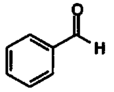
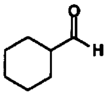
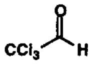
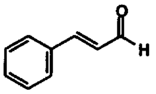
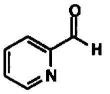
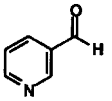
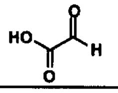
In order to ascertain that the reaction was catalyzed by CF_3SO_3H, we carried out a series of experiments to rule out alternative possibilities. (a) The same reaction when conducted in the presence of CF_3SO_3H and pyridine (100 mol%), a known proton scavenger gave no reaction. (b) No decomposition of the allyltributylstannane was observed even after stirring the allystannane with trifluoromethane sulphonic acid for 24 hours. Traces of decomposition were observed after stirring for 2 days. In effect, the catalysis of this allylstannane addition to carbonyl compounds may be totally attributed to the presence of CF_3SO_3H.



Scheme 2

After establishing that trifluoromethane sulphonic acid is the actual catalyst involved, reactions using other aldehydes were carried out. The results are summarized in Table 1.

Table 1. Reaction of allyltributyltin with various carbonyl compounds in the presence of CF_3SO_3H.[a]

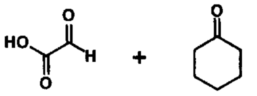
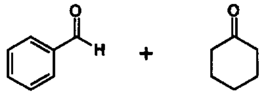
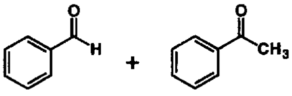
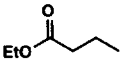
Entry	Aldehyde	Conditions	Yield%[b]
1	 3	$InCl_3$(20 mol%), H_2O, 16 h	0
2	3	$Yb(Otf)_3$(20 mol%), H_2O, 16 h	0
3	3	$La(Otf)_3$(20 mol%), H_2O, 16 h	0
4	3	CF_3SO_3H(20 mol%), H_2O, 16 h	65
5	3	CF_3SO_3H(100 mol%), H_2O, 16 h	70
6		CF_3SO_3H(100 mol%), H_2O, 16 h	72
7		CF_3SO_3H(100 mol%), H_2O, 16 h	59
8		CF_3SO_3H(100 mol%), H_2O, 16 h	62
9		CF_3SO_3H(200 mol%), H_2O, 16 h	90
10		CF_3SO_3H(200 mol%), H_2O, 16 h	85
11		CF_3SO_3H(100 mol%), H_2O, 16 h	92

a All reactions were carried out on 0.2-1 mmol scale. b Isolated yield.

In general the reactions were clean and only the excess of allyltributyltin and the homoallylic products were detected after aqueous workup. The desired homoallylic alcohols were obtained in moderate to good yields, as indicated in Table 1. Especially noteworthy is the fact that water soluble aldehydes such as glyoxylic acid can be used directly. The use of 2- and 3-pyridine carboxaldehyde requires 2 equiv. of trifluoromethane sulphonic acid since one equiv. of the trifluoromethane sulphonic acid will form a salt with the pyridine. Generally water soluble aldehydes reacted to afford the products in higher yields (entries 9, 10 & 11). Furthermore, in the case of cinnamaldehyde, only the 1,2-addition product was obtained (entries 8). The 1,4-product was not observed.

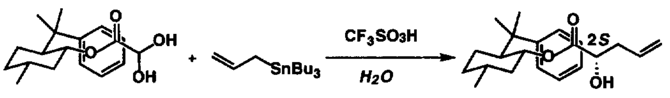
Having ascertained the efficiency of CF_3SO_3H as a good catalyst in the allylstannane addition to carbonyl compounds, we proceeded to investigate the chemoselectivity of this reaction with aldehydes in the presence of ketones. It was found that the allylation reaction was specific only to aldehydes ignoring ketone, ester and acid functional groups. The results are summarized in Table 2.

Table 2. Chemoselective Carbonyl Allylation of Aldehydes with Allytributyltin[a]

Entry	Carbonyl Compounds	Yield(%)[b]	Ratio[c]
1		90	>99:<1
2		79	>97:<3
3		75	>99:<1
4		0	

a All reactions were carried out on 0.2-1 mmol scale. b Isolated yield. c Determined by NMR.

Preliminary studies on the use of chiral aldehydes (Scheme 3) using (-)-phenylmenthol[24,25,26] as a chiral auxiliary are in progress leading to the production of compounds in moderate diastereoselectivity (2*S*:2*R* 82:18). Extension of this methodology to other allylic stannanes is now underway.



Scheme 3

In conclusion, this work demonstrates that trifluoromethane sulphonic acid catalyzed the addition of an allylstannane to carbonyl compounds in water to give the product in moderate to good yields. Furthermore, it reacted chemoselectively with aldehydes in the presence of ketones. Efforts to determine the transition states involved in these reaction by studying the effect of the geometry of the olefins on the stereochemistries of the products are in progress[27].

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