ORGANIC LETTERS

2002
Vol. 4, No. 10
1683−1685

Application of Tin and Nanometer Tin in Allylation of Carbonyl Compounds in Tap Water

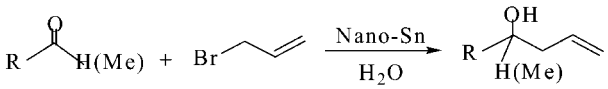
Zhiyong Wang,* Zhenggen Zha, and Cunliu Zhou

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

zwang3@ustc.edu.cn

Received February 17, 2002

ABSTRACT



Nanometer tin-mediated allylation of aldehydes or ketones in distilled or tap water gave rise to corresponding homoallyl alcohol in high yield without any other assistance such as heat or supersonic or acidic media.

With the development of industrialization, organic chemists have been confronted with a new challenge of finding novel methods in organic synthesis that can reduce and finally eliminate the impact of volatile organic solvents and hazardous toxic chemicals on the environment. So, using aqueous media to perform organic reactions has attracted considerable interest recently because water is considered to be a safe and environmentally benign solvent.[1] Allylations of aldehydes and ketones to give homoallylic alcohols are the most common reactions among these.[2] Such reactions can be achieved by use of metals such as copper/manganese,[3] calcium, and tetraallylgermane.[4] Also, all of these reactions occurred on unprotected carbohydrates in protic media under mild conditions. Nevertheless, it is necessary that most of these reactions be carried out with acidic coreagents such as ammonium chloride, hydrobromic acid, and cosolvents such as mixtures of THF and water. To simplify the allylation, chemists have been searching for effective catalysts and benign solvents under mild reaction conditions.

Nanometer materials, as we know, present remarkable electronic,[5] magnetic,[6] optical,[7] biological,[8] mechanical, and catalytic properties[9] that differ from the bulk materials. Of them, the special catalytic activities of nanomaterials intrigued our interest. Because of the larger specific surface area, the metal nanoparticle has a high surface activity, which results in a more robust catalytic activity than bulk metals. Particularly, when the nanoparticles are less than 5 nm in diameter, the catalytic activity presents special selectivity. However, to the best of our knowledge, little study has been carried out and no report about allylations catalyzed by nanometer materials has been presented yet. The following is the first report of our research on allylations catalyzed by nanometer tin in water.

To initiate the experiment, a mixture of benzaldehyde, allyl bromide, and the metal powder in 3 mL of distilled or tap water without any coreagent or cosolvent was stirred at room temperature. After about 24 h, the reaction was monitored by TLC, and the reaction mixture was extracted with ether; subsequently, the ether extract was washed with water and dried with magnesium sulfate. After removal of the solvent, the crude product was obtained. The yield of the allylation

(1) (a) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley & Sons, Inc.; New York, 1993. (b) Li, C. J. *Chem. Rev.* **1993**, *93*, 2023. (c) Chan, T. H.; Li, C. J.; Lee, M. C.; Wei, Z. Y. *Can J. Chem.* **1994**, *72*, 1181. (d) Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741. (e) Li, C. J. *Tetrahedron* **1996**, *52*, 5643. (f) Chan, T. H.; Issac, B. M. *Pure Appl. Chem.* **1996**, *68*, 919.

(2) Anastas, P., Williamson, T. C., Eds.; *Green Chemistry: Frontiers in Benign Chemical Synthesis and Processing*; Oxford University Press: New York, 1988.

(3) Li, C. J.; Meng, Y.; Yi, X. H. *J. Org. Chem.* **1997**, *62*, 8632.

(4) Akiyama, T.; Iwai, J. *Tetrahedron Lett.* **1997**, *38*, 853.

(5) Cai, Z. H.; Martin, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4138.

(6) Whitney, T. M.; Jiang, J. S.; Searson, P. C.; Chien, C. L. *Science* **1993**, *261*, 1316.

(7) Foss, C. A., Jr.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *J. Phys. Chem.* **1992**, *96*, 7497.

(8) Schmid, G. *Chem. Rev.* **1992,** *92*, 1709

(9) Lu, L.; Sui, M. L.; Lu, K. *Science* **2000**, *287*, 1463

10.1021/ol0257326 CCC: $22.00
Published on Web 04/23/2002

product was measured by ^{1}H NMR. The metals used varied from Fe to Sn, and the reaction results are listed in Table 1.

Table 1. Allylation of Benzaldehyde Mediated by Various Metals

entries	metals	yield (%)[a]/time (h)
1	Fe	polymerization
2	Mg	
3	Al	
4	Bi	35/15
5	An	20/24
6	Sn	93/15

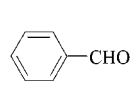
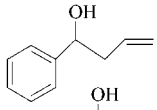
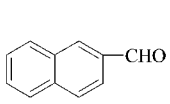
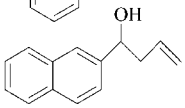
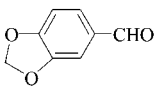
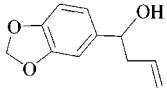
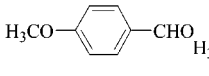
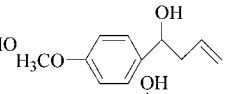
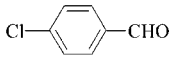
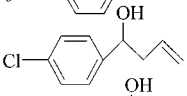
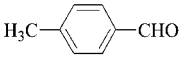
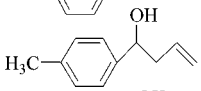
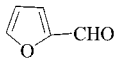
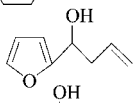
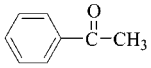
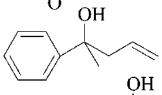
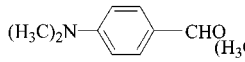
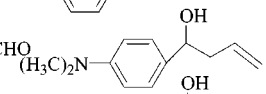
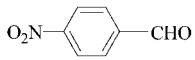
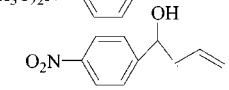
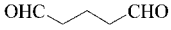
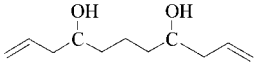
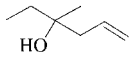
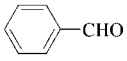
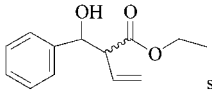
[a] Determined by ^{1}H NMR.

Polymerization occurred when the reaction was mediated by iron (entry 1, Table 1). When mediated by magnesium or aluminum, the reaction did not occur (entries 2 and 3, respectively, Table 1). In comparison with the cases that were mediated by iron, magnesium, aluminum, zinc, and bismuth, tin-mediated allylation (entry 6, Table 1) went on smoothly and obtained a high yield under the reaction conditions. This intriguing result encouraged us to investigate this tin-catalyzed reaction further. Subsequently, a variety of aldehydes and ketones were tested with this allylation method. As expected, most of the reactions were carried out smoothly in good yield, and side reactions such as reduction and coupling were not found (entries 1−7, Table 2). Moreover, the reaction conditions were sufficiently mild to not affect the methoxyl (entry 4, Table 2), chloro (entry 5, Table 2), and methyl (entry 6 Table 2) functionalities. However, allylations of acetophenone and *N*,*N*-dimethyl aminobenzaldehyde gave the corresponding products in lower yields of 40 and 33%, respectively, (entries 8 and 9, Table 2). Also, the allylations of aliphatic aldehydes or ketones did not work well under this condition (entries 11 and 12, Table 2). In particular, for 4-nitrobenzaldehyde, only N-alkylation products were observed instead of the allylation product (entry 10, Table 2). To solve these problems, after a series of investigations, nanometer tin particles were prepared[10] and applied in those allylations.

To compare the difference between ordinary tin and nano-tin in this kind of reaction, the summary of the reactions was listed in Table 2.

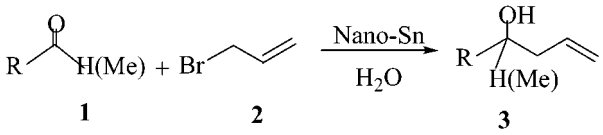
As for benzaldehyde (entry 1), 2-naphthaldehyde (entry 2), piperonal (entry 3), 4-methoxybenzaldehyde (entry 4), 4-chlorobenzaldehyde (entry 5), and 4-methyl-benzaldehyde (entry 6), the allylations can be carried out very well and finished over a short period. Especially from entries 2 to 6 in Table 2, the allylations were almost quantitative. In addition, the reaction time was reduced from 8−24 h to 1.5−8 h when compared with the those catalyzed by bulk tin powder. The aliphatic aldehydes and ketones that were generally difficult to allylate when catalyzed by tin powder can be also allylated smoothly under this condition (entries 11 and 12, Table 2). It was also noted that allylation of *N*,*N*-dimethyl aminobenzaldehyde gave the corresponding product in more than 90% yield under this condition (entry 9, Table

Table 2. Allylation Reaction Mediated by Tin[a] in Water

entries	substrates	products	yield (%)[b]/Time(h)
1			95 (93)[c]/1.5(13)
2			99 (95)/3.5(18)
3			99 (95)/3.0(17)
4			99 (95)/2.0(16)
5			99 (95)/2.0(13)
6			96 (82)/3.0(15)
7			96 (90)/3.5(13)
8			65 (40)/4.0(18)
9			95 (33)/4.0(12)
10			95(-)/5.0(20)
11			90 (60)/1.5(8)
12			85 (55)/1.5(7)
13[d]			75(71)/8(24) syn:anti 95(68):5(32)

[a] Tin was in the nanometer scale (20−30 nm). [b] Determined by ^{1}H NMR. [c] Data in brackets were mediated by regular tin powder. [d] Allyl bromide was replaced with 4-bromobutenate.

Scheme 1



(10) **Preparation of Nanometer Tin.** To 1 L of 2.0 M 2-propanol aqueous solution were added 2.25 g (0.01 mol) of $SnCl_2$ and 20 g (0.5 mol) of NaOH. The reaction mixture was stirred until the dissolution of $SnCl_2$ and NaOH. Then, a small amount of SLS (sodium lauryl sulfate) was added to this mixture. Afterward, the prepared solution was bubbled by nitrogen over about 20 min and then irradiated under a γ-ray (^{60}Co) source for about 12 h (2.5×10^4 Gy). The nano-tin was obtained from the solution by centrifugation.

2), whereas the reaction did not occur at all in distilled water when Zn, Bi, or Al was used as a mediator. As for 4-nitrobenzaldehyde, the allylation could proceed smoothly and gave about 95% yield of the desired product (entry 10, Table 2) rather than N-alkylation products, which did not give the desired product with several other methods.[11] It was noted that nano-tin changed the reaction selectivity in this situation, which was very interesting for the development of organic synthetic methodology. Meanwhile, the diastereoselectivity of the allylation catalyzed by nano-tin was studied here. The investigation was focused on the allylation of benzaldehde with ethyl 4-bromobut-2-enoate in water (entry 13, Table 2). The reactions catalyzed by ordinary tin and nano-tin both gave rise to the corresponding γ-addition product.[12] However, the ratio of syn to anti isomers was different. Benzaldehyde reacted with ethyl 4-bromobut-2-enoate in water to give rise to the syn isomer as the dominant product (92%) when catalyzed by nano-tin, whereas 68% was obtained when the reaction was catalyzed by ordinary tin. The result demonstrated that the syn isomer was a chelate-controlled product due to the hydrogen bond between the proton in hydroxyl groups and the oxygen in ester group. What is more, replacing the distilled water with tap water had no influence on the allylations. We attempted to try nano-zinc and nano-bismuth. However, nano-zinc was too active to exist in water and nano-bismuth gave rise to a mixture rather than allylation products.

This study demonstrated that the unusual phenomenon of nanometer tin-mediated allylation was caused by properties of nanometer tin particles. The smaller the radius of tin nanometer particles, the greater the ratio of surface to volume, which leads to a large increase of atoms on the surface and an abundance of suspended and unsaturated bonds and so on, affected by the unsaturated coordination. All these make the surface of the tin nanometer particle more active and enhance the reaction selectivity.

In conclusion, the result demonstrated that an efficient and clean synthesis for allylation in distilled or tap water with high product yields can be developed. Nano-tin particles were applied in the allylations of aldehyde and ketone, and satisfactory results were obtained. Our work showed us that substantial progress could be made in organic reactions in water, which have great potential in reducing chemical pollution.

Acknowledgment. The authors are grateful to National Nature Science Foundation of China (No. 50073021) and National Nature Science Foundation of Anhui Province (No. 01046301) for their support.

Supporting Information Available: Spectral data of allylation products and the TEM of nano-tin. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0257326

(11) (a) Zhang, W. C.; Li, C. J. *J. Org. Chem*. **1999**, *64*, 3230. (b) Li, C. J.; Meng, Y.; Yi, X. H. *J. Org. Chem*. **1998**, 63, 7498. (c) Chan, T. H.; Issac, M. B. *Pure Appl. Chem.* **1996**, *68*, 919. (d) We have investigated and solved this problem in another manuscript

(12) When some phase transfer catalyst was added to the reaction mixture, the α-addition product can be obtained. The result will be reported in another manuscript.