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A Recyclable Electrochemical Allylation in Water

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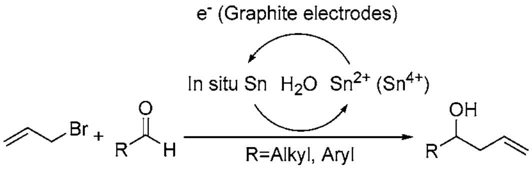
ABSTRACT



To develop environmentally benign processes for C–C bond formation, electrochemistry is applied in a tin-mediated allylation reaction in water. In this electrochemical process, the corresponding homoallylic alcohols are prepared in excellent yields, while both tin salt and water can be recycled and electrode materials are not consumed.

Organic reactions in water have been widely studied in order to minimize the use of organic solvents, many of which are flammable, toxic, or carcinogenic.[1] Electrochemical methods in organic synthesis are another approach to green chemistry[2] because they can fundamentally eliminate the waste treatment and disposal of used redox reagents.[3] Obviously, a combination of aqueous media and electrochemical conversion can utilize both advantages and provide a more efficient approach to environmentally benign processes. Metal-mediated allylation is a well-known example of organic reactions in aqueous media.[4,1a] However, excessive metal is used and the corresponding salt is generated as waste.

On the other hand, it has been reported that low-valent metal can be regenerated electrochemically in situ to mediate allylation reactions in organic solvents.[5] To develop environmentally benign processes for C−C bond formation, we applied electrochemistry in the tin-mediated allylation reaction in water. In this electrochemical process, both tin salt and water can be easily recycled and electrode materials are not consumed.[5,6] This study is detailed in the following text.

As shown in Scheme 1, our approach to the recyclable electrochemical process for tin-mediated allylation was based on the idea of using the cathode as a reducing reagent for tin(II or IV) salts. The metallic tin generated on the cathode reacts with allyl bromide to generate allyltin bromide and diallyltin dibromide, which can mediate the allylation reaction of aldehyde.[7,4a] A system of benzaldehyde, allyl bromide,

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(1) (a) Li, C. J. *Chem. Rev.* **1993**, *93*, 2023. (b) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York, 1997. (c) Lindström, U. M. *Chem. Rev.* **2002**, *102*, 2751.

(2) (a) Anastas, P. T.; Kirchhoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686. (b) Anastas, P. T.; Warner, J. C. *Green Chemistry*: *Theory and Practice*; Oxford University Press: New York, 1997.

(3) (a) Hilt, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 1720. (b) Seka, S.; Burize, O.; Nédélec, J. Y.; Périchon, J. *Chem. Eur. J.* **2002**, *8*, 2534. (c) Gomes, P.; Gosmini, C.; Périchon, J. *J. Org. Chem.* **2003**, *68*, 1142. (d) Grigg, R.; Putnikovic, B.; Urch, C. J. *Tetrahedron Lett.* **1997**, *38*, 6307. (e) Hilt, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 3586. (f) Nematollahi, D.; Rahchamani, R. A. *J. Electroanal. Chem.* **2002**, *520*, 145.

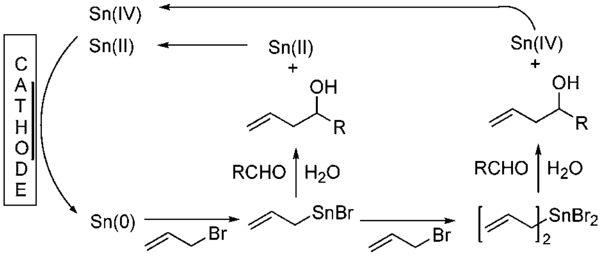
(4) For reviews on metal-mediated reactions in aqueous media, see: (a) Li, C. J. *Tetrahedron* **1996**, *52*, 5643. (b) Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741. (c) Li, C. J. *Acc. Chem. Res.* **2002**, *35*, 533.

(5) (a) Hilt, G.; Smolko, K. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3399. (b) Hilt, G.; Smolko, K. I.; Waloch, C. *Tetrahedron Lett.* **2002**, *43*, 1437.

(6) In electrochemical organic reactions, metal electrodes are often consumed sacrificially. For examples, see: (a) Durandetti, M.; Nédélec, J. Y.; Périchon, J. *Org. Lett.* **2001**, *3*, 2073.

10.1021/ol050483h CCC: $30.25

Scheme 1. Proposed Mechanism for an Electrochemical Process for Tin-Mediated Allylation of Aldehydes in Water[a]



[a] In this electrochemical process, Sn^{2+} and Sn^{4+} (from spent Sn^{2+}) were reduced at the cathode, while Sn^{2+} and Br^- were oxidized at the anode. The generated Sn^0 mediated the allylation, and the generated Br_2 was hydrolyzed in water.

and $SnCl_2$ was first tested by using cyclic voltammetry. As shown in trace c (green) in Figure 1, two cathodic peaks (C_1 and C_2, corresponding to the transformations of Sn(IV) to Sn(II) and of Sn(II) to Sn(0), respectively) and one anodic peak (A_1, corresponding to the transformation of Sn(II) to Sn(IV)) are recorded for a solution of $SnCl_2$ (5 mM) and NaBr (10 mM, as a supporting electrolyte) in water. When benzaldehyde (2.5 mM) and allyl bromide (4 mM) were added, similar peaks were recorded (shown in trace a (black) in Figure 1). Then, the electrolytic potential was determined on the basis of the reduction potential of Sn(II), which was measured by using cyclic voltammetry. After careful tests, an electrolytic potential of 2.0 v was found to be the most effective for this electrochemical allylation in water. When the electrolytic potential is below 1.5 v, no allylation product is yielded. When it is higher than 2.5 v, byproducts result from reduction and coupling reaction of benzaldehyde. It is noticed that this electrochemical allylation is also sensitive to the concentration of $SnCl_2$. If the concentration of $SnCl_2$ is lower than 1 M, no allylation product occurs at an electrolytic potential of 2.0 v. On the other hand, a higher concentration of $SnCl_2$ results in byproducts. This can be explained by considering the correlation between the reduction potential and the concentration of Sn(II), which is ruled by the Nernst equation.

A variety of aldehydes were tested in this electrochemical allylation reaction. A typical procedure is described as follows. A mixture of benzaldehyde (5.0 mmol), allyl bromide (8 mmol) and stannous chloride (10 mmol) in 10 mL of water was stirred in a round-bottom flask cell equipped with a pair of graphite electrodes at room temperature. The

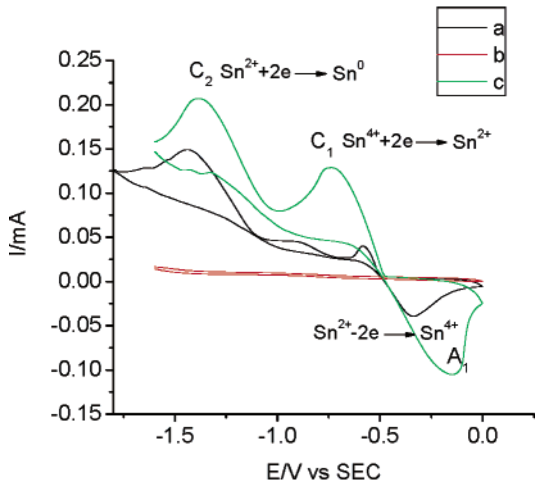
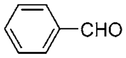
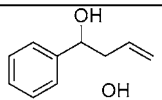
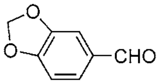
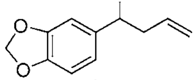
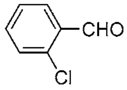
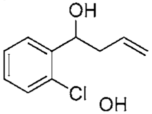
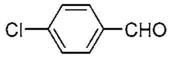
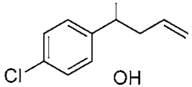
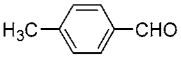
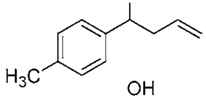
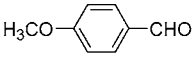
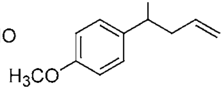
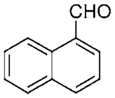
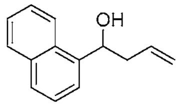
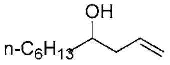
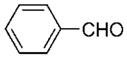
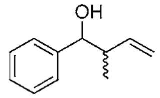
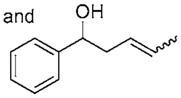


Figure 1. Cyclic voltammograms of the solution in water recorded at a scan rate of 50 mV s^{-1} and room temperature with two glassy carbon electrodes (3.0 mm diameter). Sodium bromide is applied as a supporting electrolyte: (a) 5 mM $SnCl_2$, 10 mM NaBr, 2.5 mM benzaldehyde, and 4 mM allyl bromide; (b) 10 mM NaBr only; (c) 5 mM $SnCl_2$ and 10 mM NaBr.

Table 1. In Situ Tin-Mediated Allylations of Aldehydes in Water under Electrochemical Regeneration of $SnCl_2$ Mediator

entry	substrate	product	time(h)	yield (%)
1			10	100
2[a]			6	>99
3[b]			8	96
4[b]			10	95
5			8	>99
6			8	>99
7			10	>99
8	n-C_6H_{13}CHO		6	>99
9[c]		 and 	12	99 α:γ = 31:69

[a] Concentration of $SnCl_2$ was 0.5 M. [b] In company with trace byproducts. [c] Allyl bromide was replaced with crotyl bromide.

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(7) (a) Nokami, J.; Otera, J.; Sudo, T.; Okawawa, R. *Organometallics* **1983**, *2*, 191. (b) Chan, T. H.; Yang, Y.; Li, C. J. *J. Org. Chem.* **1999**, *64*, 4452. (c) Tan, X. H.; Hou, Y. Q.; Huang, C.; Liu, L.; Guo, Q. X. *Tetrahedron* **2004**, *60*, 6129. (d) Zha, Z.; Qiao, S.; Jiang, J.; Wang, Y.; Miao, Q.; Wang, Z. *Tetrahedron* **2005**, *61*, 2521.

suspension was electrolyzed at a constant potential (2.0 v) and stirred alternately until benzaldehyde was completely consumed. Then, the reaction mixture was extracted with diethyl ether, and common workup afforded the corresponding homoallylic alcohol almost quantitatively without further purification. The results are summarized in Table 1. Both aromatic (entries 1−7 and 9 in Table 1) and aliphatic (entry 8 in Table 1) aldehydes can be allylated in this reaction. The acetal group is not hydrolyzed under these conditions (entry 2, Table 1). The regioselectivity of reaction was also investigated by replacing allyl bromide with crotyl bromide. As indicated in entry 9 of Table 1, the reaction between benzaldehyde and crotyl bromide affords the γ-adduct as the major product.

The reuse of mediator ($SnCl_2$) can be easily achieved in this electrochemical process because metallic tin is regenerated on the cathode by reducing tin(II or IV) salts, which result from the allylation reaction. To reuse the mediator, the reaction mixture is extracted with diethyl ether three times, and the remaining aqueous layer is used in the next cycle without further purification. As shown in Table 2, the allylation product is still obtained in a good yield (86%) even though the mediator is reused in the fifth cycle.

In conclusion, the study above puts forth a new approach to an environmentally benign process for metal-mediated allylation reactions by combining electrochemical conversion and aqueous media. In this electrochemical process, tin is generated in situ by electrolysis and mediates allylation reaction of aldehydes in water. Both tin salt and water can be easily reused, and electrode materials are not consumed. Further research is in progress in our laboratory to utilize this electrochemical allylation reaction in wide synthetic applications.

Table 2. Yield for Allylation of Benzaldehyde in Subsequent Cycles with the Mediator ($SnCl_2$) Reused Electrochemically

entry	mediator ($SnCl_2$)	yield (%)
1	1st cycle[a]	100
2	2nd cycle[b]	99
3	3rd cycle[b]	95
4	4th cycle[b]	85
5	5th cycle[b]	86

[a] Performed with 5.0 mmol of benzaldehyde and 8 mmol of allyl bromide in this cycle. [b] Performed with 2.5 mmol of benzaldehyde and 4 mmol of allyl bromide in this cycle.

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Supporting Information Available: Details for electrochemical reactions and characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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