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Electrochemically Supported Deoxygenation of Epoxides into Alkenes in Aqueous Solution

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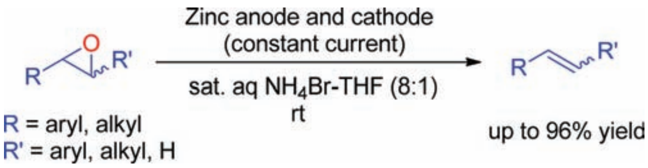
ABSTRACT



An efficient synthesis of alkenes from epoxides in a mixture of saturated aqueous NH_4Br and tetrahydrofuran (8:1) has been developed in an undivided cell fitted with a pair of zinc electrodes, and it is proposed that the reaction is mediated by Zn(0) with a hierarchically organized nanostructure.

A burst of research activity has been witnessed in recent years in the area of preparation, fabrication, and application of different sizes, shapes, and morphologies of metallic nanostructures. Due to their special activities, the application of metallic nanostructures presents a booming perspective in organic synthesis.[1] Electrochemical deposition techniques, among several other methods for the preparation of nanomaterials, are attractive because of the use of relatively inexpensive equipment and the ease of the procedures. Multidimensional nanomaterials are attracting much interest because of their potential use in many different areas;[2] however, their application in organic synthesis is rarely addressed.

Deoxygenation of epoxides into alkenes is a highly important synthetic transformation in organic and pharmaceutical chemistry, because it allows the use of the oxirane ring as a protective group for carbon–carbon double bonds.[3] Methods for this transformation have been developed for many years.[4] Recently, supported gold and silver nanoparticles[5] have been successfully applied in the catalytic synthesis of alkenes from epoxides by the use of CO/H_2O and H_2 as reductants. Electrochemical methods are an approach to efficient organic transformations and sustainable chemistry,[6] and in consequence of our interest in the preparation and application of multidimensional nanometals in organic synthesis,[7] herein we report a hierarchically organized zinc nanostructure mediated eliminative deoxygenation of epoxides in a mixture of saturated aqueous NH_4Br and THF (8:1) at rt under electrochemical conditions.

In an undivided cell, Zn foils were used as both anode and cathode.[8] Studies were initiated by screening of the electrolytes. In a neutral KNO_3 (0.1 M) /THF (8:1) solution (Table 1, entry 1), styrene oxide was not consumed completely after the electrolysis had been carried out for 1 h

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(1) (a) Shylesh, S.; Schünemann, V.; Thiel, W. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 3428–3459. (b) White, R. J.; Luque, R.; Budarin, V. L.; Clark, J. H.; Macquarrie, D. J. *Chem. Soc. Rev.* **2009**, *38*, 481–494. (c) Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Elst, L. V.; Muller, R. N. *Chem. Rev.* **2008**, *108*, 2064–2110. (d) Zhou, Y.-Q.; Zha, Z.-G.; Xu, X.-L.; Wang, Z.-Y. *Zhongguo Kexue Jishu Daxue Xuebao* **2008**, *38*, 647–655. (e) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638–643. (f) Corma, A.; Serna, P. *Science* **2006**, *313*, 332–334. (g) Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* **2006**, *311*, 362–365. (h) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, 405–408.

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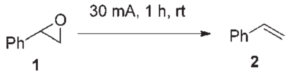
Table 1. Optimization of the Reaction Conditions for the Electrochemical Deoxygenation of Epoxides into Alkenes in Aqueous Media[a]



entry	anode–cathode	electrolyte	yield [%][b]
1	Zn–Zn	KNO_3 (0.1 M)/THF (8:1)	30
2	Zn–Zn	sat. aq NH_4HCO_3/THF (8:1)	50
3	Zn–Zn	sat. aq NH_4Cl/THF (8:1)	70
4	Zn–Zn	sat. aq NH_4Br/THF (8:1)	95
5	Zn–Zn	sat. aq NH_4Br	83
6	Zn–Zn	sat. aq NH_4Br/MeCN (8:1)	20
7	Zn–Zn	sat. aq NH_4Br/MeOH (8:1)	40
8	Zn–Zn	sat. aq NH_4Br/DMF (8:1)	30
9[c]	Zn–Zn	sat. aq NH_4Br/THF (8:1)	81
10[d]	Zn–Zn	sat. aq NH_4Br/THF (8:1)	77
11	Pt–Pt	sat. aq NH_4Br/THF (8:1)	trace
12	Al–Al	sat. aq NH_4Br/THF (8:1)	<10
13	Sn–Sn	sat. aq NH_4Br/THF (8:1)	<10

[a] Standard conditions: epoxide (0.5 mmol) in electrolyte (4.5 mL) was electrolyzed at a constant current of 30 mA in a round-bottomed flask cell equipped with a pair of zinc electrodes (1.5 cm^2) at rt. [b] Determined by GC by using an internal standard technique. [c] 15 mA. [d] 45 mA.

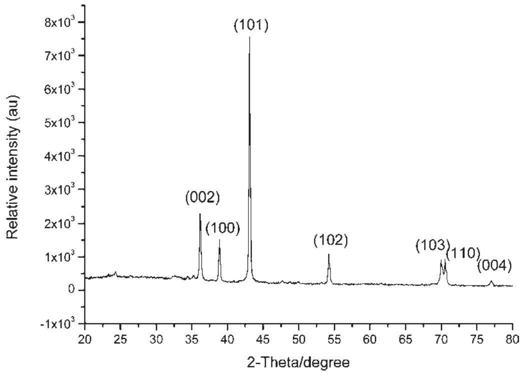


Figure 1. X-ray diffraction spectrum of Zn deposits when the electrolysis proceeded for 40 min.

and only a 30% yield of the desired product was obtained. It was observed that ammonium salts were more promising for this reaction (Table 1, entries 2–4), and NH_4Br was found to be superior (95% yield) to NH_4HCO_3 and NH_4Cl. Without THF, only an 83% yield of product was collected (Table 1, entry 5). Other organic solvents (MeCN, MeOH, and DMF) resulted in lower yields (Table 1, entries 6–8). Subsequent experiments that focused on investigating the effect of current density (Table 1, entries 9 and 10) revealed that an increase or decrease of the current resulted in a decrease in the yield. The use of other metals (Pt, Al, and Sn) instead of Zn as electrodes gave much lower yields (Table 1, entries 11–13).

The scope and limitation of the Zn-mediated deoxygenation reaction were explored next. As shown in Table 2, both the aromatic and aliphatic epoxides can be utilized in this methodology. For the aromatic epoxides **1a**, **1b**, and **1c** (Table 2, entries 1–3), alkenes can be prepared smoothly in good to excellent yields without any additives, while for epoxides **1d**–**1j** (Table 2, entries 4–10), acetic acid was added to promote the reaction and the dosage of the acid varied on different epoxides.[9] ***Z*** to ***E*** isomerization occurred during the deoxygenation process of *cis*-stilbene

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(4) For representative reports, see: (a) Mahesh, M.; Murphy, J. A.; Wessel, H. P. *J. Org. Chem.* **2005**, *70*, 4118–4123. (b) McMurry, J. E.; Silvestri, M. G.; Fleming, M. P.; Hoz, T.; Grayston, M. W. *J. Org. Chem.* **1978**, *43*, 3249–3255. (c) Kupchan, S. M.; Maruyama, M. *J. Org. Chem.* **1971**, *36*, 1187–1198. (d) Berry, M.; Davies, S. G.; Green, M. L. H. *J. Chem Soc., Chem. Commun.* **1978**, 99–100. (e) Bertini, F.; Grasselli, P.; Zubiani, G.; Cainelli, G. *J. Chem. Soc., Chem. Commun.* **1970**, 144–145. (f) Ledon, H.; Tkatchenko, I.; Young, D. *Tetrahedron Lett.* **1979**, 173–176. (g) Clive, D. L. J.; Denyer, C. V. *J. Chem. Soc., Chem. Commun.* **1973**, 253–254. (h) Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112–127. (i) Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538–6540. (j) Giering, W. P.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1972**, *94*, 7170–7172. (k) Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1971**, *93*, 4070–4072. (l) Hanson, J. R. *Synthesis* **1974**, 1–3. (m) Fujisawa, T.; Sugimoto, K.; Ohta, H. *Chem. Lett.* **1974**, 883–886. (n) Santos, R. B.; Brocksom, T. J.; Brocksom, U. *Tetrahedron Lett.* **1997**, *38*, 745–748. (o) Patra, A.; Bandyopadhyay, M.; Mal, D. *Tetrahedron Lett.* **2003**, *44*, 2355–2357. (p) Concellón, J. M.; Bardales, E. *Org. Lett.* **2002**, *4*, 189–191. (q) Schobert, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 855–856. (r) Martin, M. G.; Ganem, B. *Tetrahedron Lett.* **1984**, *25*, 251–254. (s) Choi, K. H.; Choi, K. I.; Kim, J. H.; Yoon, C. M.; Yoo, B. W. *Bull. Korean Chem. Soc.* **2005**, *26*, 1495–1496. (t) Firouzabadi, H.; Iranpoor, N.; Jafarpour, M. *Tetrahedron Lett.* **2005**, *46*, 4107–4110. (u) Oh, K.; Knabe, W. E. *Tetrahedron* **2009**, *65*, 2966–2974. (v) Iranpoor, N.; Firouzabadi, H.; Jamalian, A. *Tetrahedron* **2006**, *62*, 1823–1827. (w) Justicia, J.; Jiménez, T.; Morcillo, S. P.; Cuerva, J. M.; Oltra, J. E. *Tetrahedron* **2009**, *65*, 10837–10841.

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(8) For use of sacrificial Zn (and Mg) anodes to make active surface for organic transformations, see: Lombardo, M.; Trombini, C. The Chemistry of Zinc Enolates. In *The Chemistry of Organozinc Compounds*; Rappoport, Z., Marek, I., Eds.; John Wiley & Sons: Ltd.: Chichester, U.K., 2007; Chapter 18, pp 797–861, and references cited therein.

(9) For the reaction of cyclohexene oxide, a mixture of cyclohexanol, cyclohexane-1,2-diol, and cyclohexane was obtained as the side products.

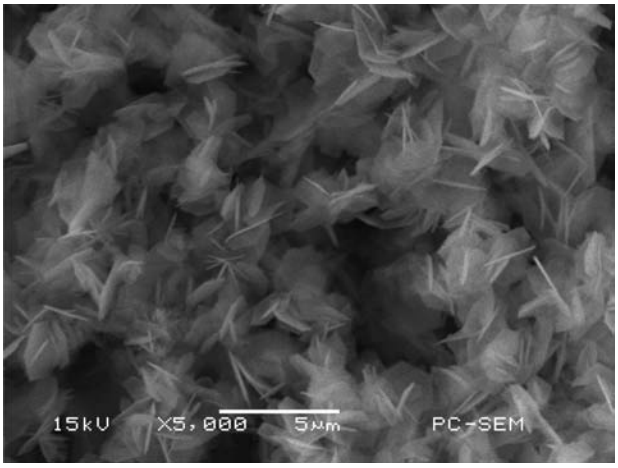
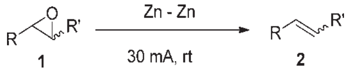


Figure 2. SEM image of Zn deposits when the electrolysis proceeded for 40 min.

oxide **1e**, and the product ratio of *trans*-stilbene and *cis*-stilbene was 95:5 (Table 2, entry 5) as determined by a crude ^{1}HNMR. The deoxygenation of a long chain aliphatic epoxide was not as effective as aromatic epoxides, and more THF was needed[10] (Table 2, entry 9). In the cases of substrates with an ether and ester functional group (Table 2, entries 6 and 7), alkenes were prepared smoothly in excellent yields, while the ketone (Table 2, entry 10) was not compatible with our deoxygenation conditions and only 13% of desired product was obtained.[11]

In order to obtain information concerning the reaction pathways and mechanism of the epoxide deoxygenation under electrochemical conditions, further studies were undertaken. As observed, an almost equimolar amount of Zn was consumed[12] for every mole of styrene oxide conversion; hence it was proposed that the reaction was mediated by Zn(0) deposited on the cathode.[13] We then studied the deoxygenation of epoxides using commercial Zn powder in sat. aq NH_4Br/THF (8:1) under nonelectrochemcial conditions. After the solution was stirred for 1 h, only a 43% yield of alkene was obtained. Next, we investigated the reaction by using inert Pt as electrodes and adding commercial Zn powder to sat. aq NH_4Br/THF (8:1), and the yield of the deoxygenated product was 46%. This demonstrated that the normal Zn powder was not a good mediator for this reaction, and the electroreductive deoxygenation on the cathode was neglectable although the reductive wave was observed for styrene oxide by cyclic voltammetry studies.[14]

Table 2. Electrochemical Deoxygenation of Epoxides into Alkenes in Aqueous Media[a]



entry	R	R′	HOAc [μL]	product	yield [%][b] (time [h])
1	Ph	H	0	**2a**	96[c] (1)
2	4-Br-C_6H_4	H	0	**2b**	86 (1)
3	Naph	H	0	**2c**	90 (1)
4	Ph (*E*)	Ph	40	**2d**	95 (3)
5	Ph (*Z*)	Ph	80	**2d**, **2e**	95 *E*:*Z* 95:5 (4)
6	EtO_2C	Ph	80	**2f**	90 (2.5)
7	4-MeO-$PhOCH_2$	H	160	**2g**	96 (3)
8	R = R′= $(-CH_2-)_4$		80	**2h**	71[c] (1)
9[d]	$CH_3(CH_2)_9$	H	240	**2i**	91 (4.5[e])
10	PhC(=O)	Ph	120	**2j**	13 (2)

[a] Standard conditions: epoxide (0.5 mmol), electrolyte (sat. aq NH_4Br/THF (8:1), 4.5 mL), constant current (30 mA), zinc electrodes (1.5 cm^2), rt. [b] Isolated yield. [c] Determined by GC by using an internal standard technique. [d] Electrolyte: 0.375 M *n*-Bu_4NBr in THF/H_2O (24:1), constant current (20 mA). [e] The reaction mixture was stirred for an additional 3 h after the electrolysis was stopped.

Subsequently, the deposition of Zn(0) on the cathode during the process of the deoxygenation reaction was studied by XRD and SEM. Figures 1 and 2 show the deposited Zn after the electrolysis had proceeded for 40 min. As the XRD results reveal in Figure 1, all of the diffraction peaks were identified as those of Zn(0) and the deposits were in good crystalline condition. The SEM image displayed in Figure 2 shows that the Zn is composed of a large number of nanothin sheets organized in a hierarchical structure, and the thickness of the nanosheets ranged from 70 to 100 nm.[15] Although it was not in a well-defined shape and structure, it can be observed that the internal cross-linked structure of the Zn nanosheets would effectively

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(10) The reaction carried out in anhydrous THF gave no desired product, and starting material was recovered.

(11) Other components in the product mixture were determined as starting material (about 60%) and some unidentified compounds. For the aliphatic epoxide 1-(3-pentyloxiran-2-yl)ethanone which bears a ketone group, no desired product was obtained and 37% of the starting material was recovered with side product 4-hydroxynonan-2-one from reductive ring opening of epoxides in 53% yield after the reaction had proceeded for 3 h.

(12) The weight of the anode decreased by ~60 mg (1 mmol) and that of the cathode increased by ~32 mg (0.5 mmol) after the reaction finished.

(13) Studies on the product yield vs reaction time showed that there was an induction period for the reaction (~6 min) that accounted for the formation of the Zn deposits. For further details, see the Supporting Information.

(14) For further details, see the Supporting Information.

(15) For SEM images with high magnification, see the Supporting Information.

(16) For the SEM images, see the Supporting Information.

(17) The Zn deposits were collected when the electrolysis had proceeded for 40 min and were subsequently subjected to the deoxygenation of styrene epoxide under nonelectrochemical conditions. The desired product was obtained in 95% yield base on the conversion; see the Supporting Information for details.

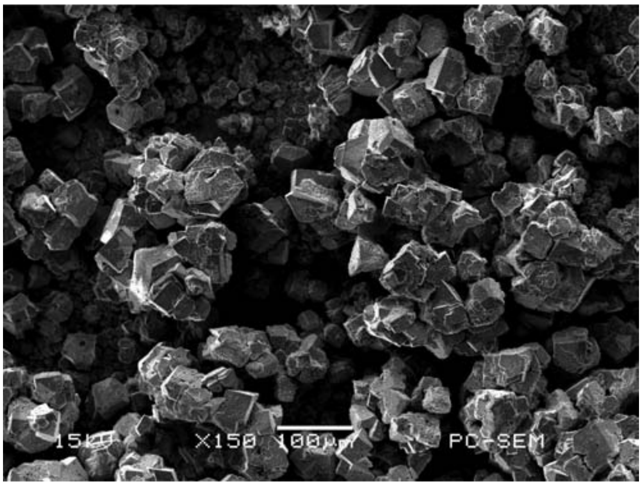

Figure 3. SEM image of Zn particles when the electrolysis proceeded for 1.5 h.

prevent lamella aggregation and maintain the long-standing existence of the hierarchitecture. It was proposed that the hierarchical structures were formed due to the formation of the complex of Zn^{2+} with epoxide.

Figure 3 shows the SEM of the deposition of Zn(0) on the cathode when the electrolysis proceeded for 1.5 h. The zinc particles were in much larger sized blocks (10−50 μm).[15] At this point, the epoxide had been completely consumed. We also studied the cathode surface by SEM when the electrolysis proceeded for 40 min in sat. aq NH_4Br/THF (8:1) without styrene oxide, and the Zn particles were in blocks (2−4 μm) too.[16] Based on the above observation, it was hypothesized that the electrochemical deoxygenation which was carried out in sat. aq NH_4Br/THF (8:1) was mediated by the fairly active[17] and stable Zn[18] with multidimensional nanostructures, which was formed by the cathodic reduction of the complex **3** as elucidated in Figure 4. Obviously, there were potentially multiple steps for the transformation of epoxide to alkene, where zinc metal could participate in two instances of single electron transfer (SET) to form anionic species **5**, which in turn collapsed to give the alkene **2**.

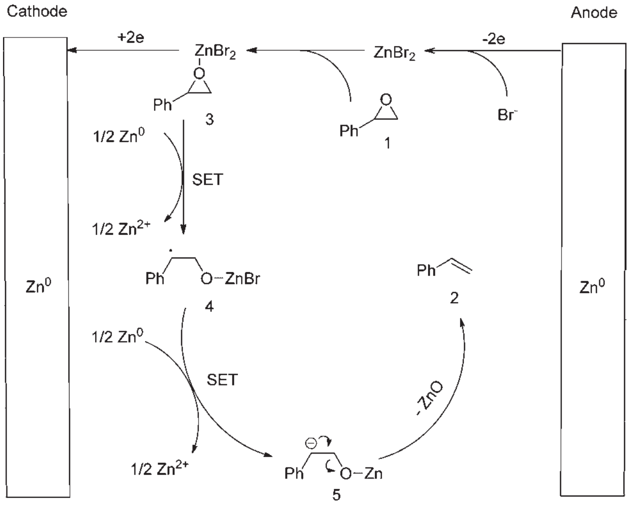

Figure 4. Proposed reaction pathway for the electrochemical process.

In conclusion, an efficient synthesis of alkenes from epoxides in sat. aq NH_4Br/THF (8:1) solution under electrochemical conditions has been developed. A hierarchically organized zinc nanostructure was obtained by electrochemical reduction of the complex of epoxide with Zn^{2+}. The as-prepared Zn mediated the reaction of the deoxygenation of epoxides *in situ* smoothly to produce alkenes in good yields. Undivided-cell equipment and rough metals were used to undergo an open-air reaction in a readily available electrolyte at rt. The simplicity and environmental friendliness of the electrolysis procedure make it an attractive alternative for the deoxygenation of epoxides. Further investigation to determine the mechanism of this reaction and to expand its scope is underway in our laboratory.

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Supporting Information Available. Spectral data of deoxygenation products, cyclic voltammetry of styrene oxide, the SEM and XRD of zinc. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) It had also been reported that the preprepared (or commercially available) nano zinc particles in zero dimension was too active to be controlled in some reactions, see: (a) Lipshutz, B. H.; Abela, A. R.; Bošković, Ž. V.; Nishikata, T.; Duplais, C.; Krasovskiy, A. *Top. Catal.* **2010**, *53*, 985–990. (b) Wang, Z.; Zha, Z.; Zhou, C. *Org. Lett.* **2002**, *4*, 1683–1685.