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Oxidative Hydroxylation Mediated by Alkoxysulfonium Ions

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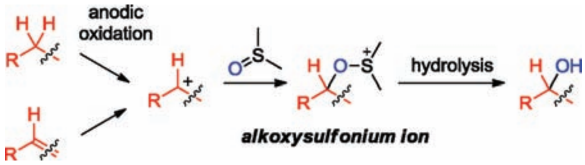
ABSTRACT



Oxidative hydroxylation of toluene derivatives via alkoxysulfonium ion intermediates was achieved by integration of anodic oxidation and hydrolysis to give benzyl alcohols which are also susceptible to oxidation. Alkenes were also oxidized to give 1,2-diols without overoxidation. The integration of electrochemical oxidative cyclization and hydrolysis was achieved using alkenes bearing a nitrogen atom in an appropriate position to give cyclic β-amino-substituted alcohols.

Combining multiple steps without isolating intermediates is important to enhance the power and efficiency of organic synthesis.[1,2] The integration of chemical reactions enables synthetic transformations that would be otherwise very difficult or impossible, such as transformations involving the generation of unstable highly reactive species that are swiftly utilized for a subsequent reaction before they decompose.[3]

Oxidation of organic compounds to products that are susceptible to oxidation provides a challenge for organic synthesis. Because products are exposed to the oxidation conditions, significant amounts of undesired overoxidation products are formed during the course of the reaction.[4] Thus, access to a general oxidation method which prevents overoxidation is highly desirable.

Electrochemical reactions using electron transfer on the surface of the electrode serve as a powerful means of selective oxidation.[5,6] Electrochemistry allows for the selective removal of electrons under mild conditions. However, the electrochemical oxidation also often suffers from overoxidation.[7] For example, anodic oxidation of alkenes and that of 1,2-diols often lead to carbon−carbon bond cleavage.[7a,b]

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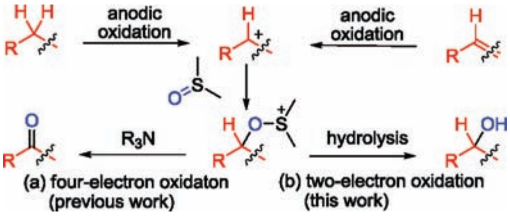
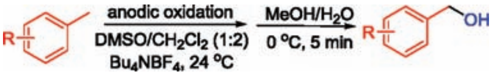
We have developed the "cation pool" method using low-temperature electrochemical oxidation.[8–10] Based on the "cation pool" method, we have recently reported alkoxysulfonium ion mediated integrated electrochemical–chemical oxidation, which solves the formidable overoxidation problem (Scheme 1a).[11] Electrochemically generated carbocations are converted to the alkoxysulfonium ions, which give the corresponding carbonyl compounds by treatment with amines. We envisioned that hydrolysis of the electrochemically generated alkoxysulfonium ions would give the corresponding alcohols (Scheme 1b). Because the oxidation step (electrolysis) and the alcohol-forming step (hydrolysis) are separated, the products are not exposed to the oxidation conditions and overoxidation should not occur. This integrated hydroxylation reaction and previously reported integrated electrochemical–chemical oxidation to carbonyl compounds are complementary. Herein we report on the aforementioned oxidation reaction via electrochemical oxidation to give alkoxysulfonium ions and their hydrolysis.

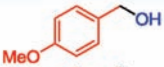
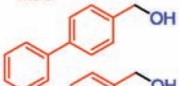
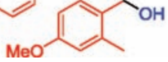
Scheme 1. Selective Oxidation Mediated by Alkoxysulfonium Ion



First, we began by studying the oxidation of toluenes to benzyl alcohols.[12] Toluenes were electrochemically oxidized in the presence of DMSO in CH_2Cl_2 using Bu_4NBF_4 as a supporting electrolyte at rt. A divided cell equipped with a C-felt anode and a Pt-plate cathode was used. After electrolysis, the resulting solution was hydrolyzed by aqueous NaOH or $MeOH/H_2O$ at 0 °C to give the corresponding benzyl alcohols in good yields (Table 1).

Table 1. Integrated Oxidation–Hydrolysis of Toluenes[a]



entry	electricity (F/mol)	product	yield (%)[b]
1[c]	2.1		85
2	5.0		60
3	2.5		74
4	2.5		72

[a] Reactions were carried out on a 0.25 mmol scale. [b] Isolated yield after chromatography. [c] Hydrolyzed by aqueous NaOH.

In general, electrochemical benzylic monohydroxylation is quite difficult because the products are also oxidized to give benzaldehyde and benzoic acid.[7c,13] In fact, the oxidation potential of 4-methoxybenzyl alcohol (1.42 V vs SCE) lies close enough to that of 4-methoxytoluene (1.38 V vs SCE)[14] to make selective oxidation of the toluene near impossible. However, the present transformation enables direct oxidation of toluenes to benzyl alcohols with high selectivity. Presumably a positive charge in the alkoxysulfonium ion retards further oxidation by raising the oxidation potential.[15] Alternatively, overoxidation is prevented because a positively charged alkoxysulfonium ion cannot readily approach a positively charged anode. Interestingly, toluenes having more than two methyl groups were selectively oxidized to monoalcohols (Table 1, entries 3 and 4). Prevention of the oxidation of the second methyl group can also be attributed to the positive charge of the alkoxysulfonium ion intermediate.

Next, we examined oxidative dihydroxylation of alkenes.[16] *trans*-Stilbene was electrochemically oxidized in the presence of DMSO to give the bisalkoxysulfonium ion, whose structure was determined by ^{1}H NMR spectroscopy. Hydrolysis

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(9) Alkoxycarbenium ion pools: (a) Suga, S.; Suzuki, S.; Yamamoto, A.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 10244. (b) Okajima, M.; Suga, S.; Itami, K.; Yoshida, J. *J. Am. Chem. Soc.* **2005**, *127*, 6930. (c) Suga, S.; Matsumoto, K.; Ueoka, K.; Yoshida, J. *J. Am. Chem. Soc.* **2006**, *128*, 7710.

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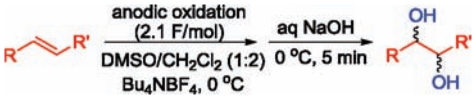
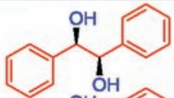
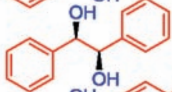
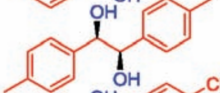
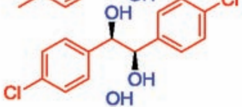
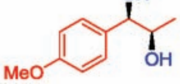
(14) The oxidation potentials were measured by RDE in $LiClO_4/CH_3CN$ using an SCE as a reference electrode. See Supporting Information.

(15) In the presence of DMSO, a substrate having a higher oxidation potential than that of DMSO is not electrolyzed. See ref 11.

with aqueous NaOH gave the corresponding 1,2-diol, hydrobenzoin, in 75% yield with high diastereoselectivity ($R^*R^*/R^*S^* = 93{:}7$) (Table 2, entry 1). *cis*-Stilbene gave the same stereoisomer preferentially, although the diastereoselectivity was lower ($R^*R^*/R^*S^* = 66{:}34$) (entry 2).

Table 2. Integrated Oxidation−Hydrolysis of Alkenes[a]



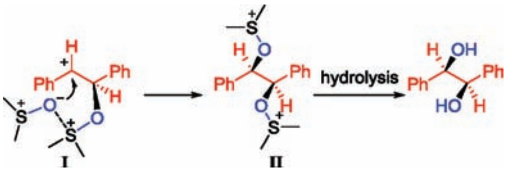
entry	major product	yield (%)[b]	dr[c]
1		75	93/7
2[d]		69	66/34
3		72	87/13
4		86	91/9
5		52	62/38

[a] Reactions were carried out on a 0.25 mmol scale. [b] Isolated yield after chromatography. [c] Determined by ^{1}H NMR. [d] *cis*-Stilbene was used.

Other stilbene derivatives underwent dihydroxylation under the same conditions with similar diastereoselectivity (entries 3 and 4). A β-methylstyrene derivative was also oxidized to give the corresponding diol, although the yield and diastereoselectivity were lower (entry 5). To the best of our knowledge, this is the first example of the direct electrochemical dihydroxylation of alkenes.[17] Although a variety of methods for dihydroxylation of alkenes have been reported, a highly toxic osmium catalyst[18] or explosive peroxides[19] are required in many cases. This present method, however, serves in a mild and environmentally benign manner in the dihydroxylation of alkenes.

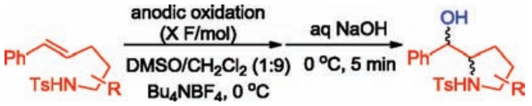
Based on the diastereoselectivity observed, we propose a mechanism shown in Scheme 2, although the details are not clarified as yet. Presumably intermediate **I** is formed by two-electron oxidation. A conformation in which two phenyl groups are apart is favorable. The sulfonium ion moiety in **I** directs the attack of the second DMSO to give bisalkoxysulfonium ion **II**,[20] which gives the diol upon hydrolysis.[21]

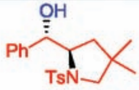
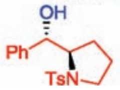
Scheme 2. Proposed Mechanism for Stereoselective Dihydroxylation of Alkenes



Finally, we applied this present oxidation method to intramolecular alkene cyclization, which assists a powerful synthetic method for the construction of heterocyclic compounds.[22,23] Electrolysis and subsequent hydrolysis of β-alkyl styrenes having a nitrogen nucleophilic moiety in an appropriate position elicited cyclization to give the corresponding alcohols having a pyrrolidine ring in high yields (Table 3). Interestingly, the reaction of (*E*)-alkenes gave the *anti*-addition product selectively (Table 3, entries 1 and 2), although the reaction of the (*Z*)-alkene gave a 1:1 mixture (Table 3, entry 3).

Table 3. Integrated Oxidation−Hydrolysis of Alkenes Bearing a Nitrogen Nucleophilic Moiety[a]



entry	electricity (F/mol)	major product	yield (%)[b]	dr[c]
1	2.1		79[d]	-[e]
2	2.1		80	90/10
3[f]	2.5		79	51/49

[a] Reactions were carried out on a 0.13 mmol scale. [b] Isolated yield after chromatography. [c] Determined by ^{1}H NMR. [d] The product was isolated by recrystallization. [e] A small amount of the other diastereomer seemed to be formed as a byproduct, although it was not fully identified. [f] *cis*-Isomer of starting material was used.

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(16) For recent advances within the area: (a) Plietker, B.; Niggemann, A.; Pollrich, A. *Org. Biomol. Chem.* **2004**, *2*, 1116. (b) Emmanuvel, L.; Shaikh, T. M. A.; Sudalai, A. *Org. Lett.* **2005**, *7*, 5071. (c) Plietker, B.; Niggemann, A. *J. Org. Chem.* **2005**, *70*, 2402. (d) de Boer, J. W.; Brinksma, J.; Browne, W. R.; Meetsma, A.; Alsters, P. L.; Hage, R.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 7990. (e) Oldenburg, P. D.; Que, L., Jr. *Catal. Today* **2006**, *117*, 15. (f) Li, Y.; Song, D.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 2962. (g) Plietker, B.; Neisius, N. M. *J. Org. Chem.* **2008**, *73*, 3218. (h) de Boer, J. W.; Brinksma, J.; Browne, W. R.; Harutyunyan, S. R.; Bini, L.; Tiemersma-Weyman, T. D.; Alsters, P. L.; Hage, R.; Feringa, B. L. *Chem. Commun.* **2008**, 3747. (i) Wang, A.; Jiang, H.; Chen, H. *J. Am. Chem. Soc.* **2009**, *131*, 3846. (j) Wang, W.; Wang, F.; Shi, M. *Organometallics* **2010**, *29*, 928. (k) Seayad, J.; Seayad, A. M.; Chai, C. L. L. *Org. Lett.* **2010**, *12*, 1412.

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(18) (a) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (b) Dobler, C.; Mehltretter, G. M.; Sundermeier, U.; Beller, M. *J. Organomet. Chem.* **2001**, *621*, 70.

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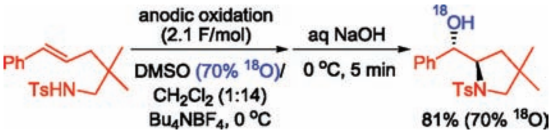
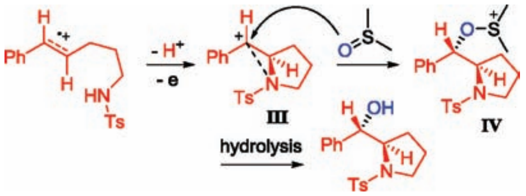
To gain deeper insight into the mechanism, an experiment using ^{18}O-labeled DMSO (containing 70% ^{18}O) was conducted.[24] The product containing ^{18}O (70% ^{18}O) was obtained in 81% yield as shown in Scheme 3. It indicates that the oxygen atom of the hydroxyl group in the product is derived from the oxygen atom of DMSO. Therefore, the C−O bond in the alkoxysulfonium ion intermediate was not cleaved. Instead, the O−S bond was cleaved upon hydrolysis. This means that the inversion of configuration at the benzylic carbon is not plausible.

Scheme 3. Mechanistic Study Using ^{18}O-DMSO



A mechanism involving formation of a bisalkoxysulfonium ion followed by internal S_N2 displacement by the amino group seems to be a reasonable explanation for the stereoselectivity. However, a mechanism involving the cationic intermediate stabilized by the intramolecular interaction with the amino group[25] seems to be more plausible (Scheme 4), because the oxidation potential of the substrate is lower than those of simple alkyl-substituted styrenes.[26] Thus, the cation radical generated by one-electron oxidation undergoes an intramolecular nucleophilic reaction with a nitrogen atom. After deprotonation an additional one-electron oxidation takes place to give the benzyl cation intermediate **III** having a conformation in which the benzylic cation center interacts with the amino group as well as the phenyl group and the alkyl chain are apart from each other. The backside attack of DMSO gives the alkoxysulfonium ion intermediate **IV**, which gives the product upon hydrolysis.

Scheme 4. Proposed Mechanism for Stereoselective Cyclization



In conclusion, we have developed a novel oxidative hydroxylation mediated by electrochemically generated alkoxysulfonium ions. Toluenes are oxidized to benzyl alcohols, and alkenes to 1,2-diols stereoselectively. In addition, the method can be applied to intramolecular alkene cyclization to give alcohols bearing a pyrrolidine ring. The intermediacy of alkoxysulfonium ions allows selective oxidation of substrates to alcohols which are easily oxidized under conventional conditions. The integrated hydroxylation reaction and previously reported integrated electrochemical−chemical oxidation to carbonyl compounds can be used in a complementary way. Further work to explore the full scope of the present approach and its applications to the synthesis of molecules with interesting functions is in progress.

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Supporting Information Available. Experimental procedures and special data for key compounds. This material is available free of charge via Internet at http://pubs.acs.org.

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(20) ^{1}H NMR analysis indicated that the bisalkoxysulfonium ion was obtained as a single stereoisomer. See ref 11 and its Supporting Information.

(21) It was reported that an optically pure alcohol was obtained by hydrolysis of an optically pure alkoxysulfonium ion. See: Ray, D. G., III; Koser, G. F. *J. Am. Chem. Soc.* **1990**, *112*, 5672.

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