Electrogenerated Acid as an Efficient Catalyst for Alcoholyses and Hydrolyses of Epoxides

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The electrochemical transformation of different epoxides to their corresponding β-alkoxy alcohols and diols was achieved by using an electrogenerated acid-catalyst. A competitive ring-opening reaction of activated epoxides in the presence of deactivated epoxides was also successfully carried out in both alcohols and water.

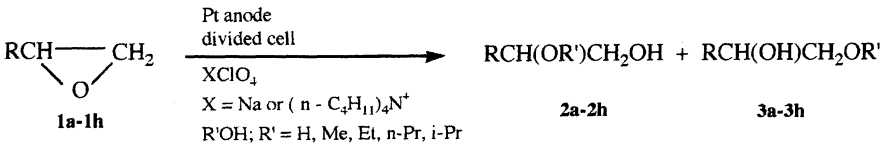
Epoxides are versatile intermediates in organic synthesis, and their ring-opening reactions with different nucleophiles in the presence of different catalysts have been extensively studied.[1—7] The electrochemical oxidation of organic compounds under both controlled-potential or constant-current conditions has achieved a great number of applications in both laboratory and industrial syntheses.

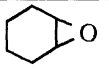
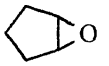
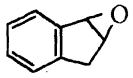
Epoxides are also known to be electroactive at both the cathode[8] and anode.[9] The anodic behavior of epoxides has been studied in nonnucleophilic solvents, such as super-dry acetonitrile. Under these conditions, isomerization to their corresponding carbonyl compounds has been reported to occur through the formation of an oxiran-2-ylium radical cation.[9] Although anodic reactions of epoxides in aprotic solvents have been reported, there has been no report, as far as we know from the literature, concerning this reaction in protic solvents, such as alcohols and water. Electrogenerated acid-catalyzed reactions have been successfully applied to some important synthetic transformations, such as, the rearrangement of some strained-ring systems,[10] the hemiacetalization of α-hydroxy ketones,[11] the protection and deprotection of alcohols with dihydropyran,[12] and the transformation of epoxides to ketones and α,β-isopropylidenedioxy copmounds.[13]

We now wish to report efficient anodic alcoholyses and hydrolyses of epoxides to their corresponding β-alkoxy alcohols or diols in excellent yields and with high regio- and chemoselectivity. Both linear and branched alcohols can be used as solvents and nucleophiles for this transformation (Scheme 1).

The reaction of styrene oxide in water, as well as in both linear and branched alcohols, was efficiently performed in a divided cell equipped with a platinum cathode and a platinum anode using sodium or tetrabutylammonium perchlorate as the supporting electrolyte under both controlled-potential and constant-current conditions. The corresponding β-alkoxy alcohols (Table 1, Entries 1—4) and 1-phenyl-1,2-ethandiol (Table 1, Entry 5) were obtained in 90—98% yields. The minimum required potential for methanolyses of epoxides was found to be +1.1 V versus saturated calomel electrode. Below this potential, no acid was generated, and the epoxide remained unreacted. The potential which was applied in 1-propanol, 2-propanol and aqueous acetonitrile was +1.5 V. These potentials were lower than those which have been reported for anodic isomerization of epoxides to ketones (+1.9—2.5 V).[9] The current efficiency was very satisfactory in these reactions; 0.0026 F mol^{-1} of electricity was passed for methanolyses of styrene oxide. As the nucleophilicity of the alcohol was decreased duo to an increase in the alkyl group bulk hinderence,[14] slight increases in the reaction time and amount of consumed electricity were observed. The F mol^{-1} values in ethanol, 1-propanol and 2-propanol were found to be 0.0033, 0.0035, and 0.0038, respectively. The F mol^{-1} value in aqueous acetonitrile was found to be 0.0067 for hydrolyses of styrene oxide to the corresponding diol. The reactions of styrene oxide in different alcohols and aqueous acetonitrile under constant-current conditions were also found to be very efficient; similar catalytic amounts of electricity were required to bring about its alcoholyses and hydrolyses at room temperature and in quantitative yields. In order to show that this is an electrogenerated acid catalysis reaction, a solution of electrolyte in methanol was preelectrolyzed for 5 min. The addition of styrene oxide to this solution afforded the corresponding β-methoxy alcohol in quantitative yield after 15 min. Next, the reaction was successfully extended to various epoxides, including those with electron-withdrawing groups (**1c**—**1e**), in different classes of alcohols and water. Some representative results are given in Table 1. The reaction of cyclic epoxides showed a high stereoselectivity along with the formation of a trans isomer.

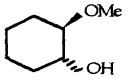
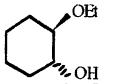
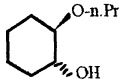
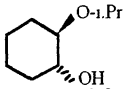
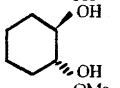
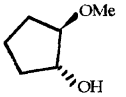
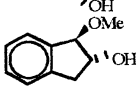
In order to examine the selectivity of this method we carried out some competitive reactions between some



R on Epoxide **1a—1e**		Epoxide **1f—1h**	
a	Ph–	**f**	
b	CH_3–		
c	$ClCH_2$–	**g**	
d	$PhOCH_2$–	**h**	
e	CH_2=$CHCH_2OCH_2$–		

Scheme 1.

Table 1. Electrogenerated Acid-Catalyzed Ring-Opening Reaction of Epoxides in Alcohols and Water

Entry	Epoxide	R'OH[a]	Product[b]	F mol^{-1} (Electrolysis time/min)	Reaction[c] time/min	Yield[d] %	bp (°C)/Torr, mp (°C) or n_D^{20} Found	Reported
1	**1a**	MeOH	**2a**	0.0026 (5)	15	98	60/2	75/0.7[15]
2	**1a**	EtOH	**2a**	0.0033 (5)	20	96	1.5143	1.5145[6,7]
3	**1a**	1-PrOH	**2a**	0.0035 (8)	20	98	1.5106	1.5108[6,7]
4	**1a**	2-PrOH	**2a**	0.0038 (8)	20	95	1.5072	1.5073[6,7]
5	**1a**	H_2O/CH_3CN	**2a**	0.0067 (5)	20	90	65—66	65—67[16]
6	**1b**	H_2O/CH_3CN	**2b**	0.0085 (8)	80	85	188/760	189/760[17]
7	**1c**	MeOH	**3c**	0.046 (60)	360	92	97—100/9	105—106[7,18]
8	**1c**	1-PrOH	**3c**	0.051 (60)	400	93	1.4375	1.4378[7,17,18]
9	**1d**	MeOH	**3d**	0.042 (60)	360	95	120—121/3	128/5[19]
10	**1d**	2-PrOH	**3d**	0.05 (65)	360	93	1.4975	1.4974[6,7]
11	**1e**	MeOH	**3e**	0.05 (65)	360	90	1.4459	1.4460[20]
12	**1f**	MeOH		0.0031 (5)	60	96	100—101/60	107—111/65[21]
13	**1f**	EtOH		0.0035 (5)	60	94	72—75/11	80—85/15[21,22]
14	**1f**	1-PrOH		0.004 (6)	70	90	86—87/10	92—96/14[21]
15	**1f**	2-PrOH		0.0045 (8)	70	91	80—81/16	89—93/18[21]
16	**1f**	H_2O/CH_3CN		0.008 (8)	70	86	102—103	105[23]
17	**1g**	MeOH		0.0035 (5)	60	95	173	175[24]
18	**1h**	MeOH		0.0031 (5)	20	93	146—147/11	146—148/11[25]

a) Aqueous H_2O/CH_3CN (1 : 1.5) was used. b) The product was isolated and compared with authentic sample. c) The reaction mixture was stirred at room temperature after stopping electrolysis. d) Yields refer to isolated products.

classes of epoxides. The results are shown in Table 2.

According to these results, the competitive reactions between activated epoxides (those with alkyl or aryl group, e.g., **1a**,**f**) and deactivated epoxides (those with electron-withdrawing groups, e.g., **1c**,**d**) in different alcohols showed excellent selectivity. Activated epoxides in the presence of deactivated ones reacted quantitatively to produce their corresponding β-alkoxy alcohols or diols; deactivated epoxides remained almost unreacted. Although some competitive selectivity was ob-

Table 2. Competitive Anodic Alcoholyses of Epoxides

Entry	Epoxide	R'OH[a)]	F mol^{-1}(Electrolysis time/min)	Reaction[b)] time/min	% of Conversion[c)]
1	**1a**+**1c**	MeOH	0.003 (6)	25	100% of **1a** 5% of **1c**
2	**1a**+**1c**	EtOH	0.004 (6)	30	100% of **1a** 3% of **1c**
3	**1a**+**1d**	MeOH	0.003 (6)	25	100% of **1a** 4% of **1d**
4	**1c**+**1f**	MeOH	0.0035 (6)	70	100% of **1f** 2% of **1c**
5	**1c**+**1f**	EtOH	0.004 (6)	70	100% of **1f** 3% of **1c**
6	**1d**+**1f**	MeOH	0.0035 (6)	70	100% of **1f** 5% of **1d**
7	**1a**+**1c**	H_2O/CH_3CN	0.007 (25)	100	100% of **1a** 0% of **1c**
8	**1a**+**1f**	MeOH	0.003 (6)	25	65% of **1a** 35% of **1f**

a) H_2O/CH_3CN (1:1.5). b) The reaction mixture was stirred at room temperature. c) Yield% of conversion was based on GLC analysis.

served between **1a** and **1f** (Table 2, Entry 8), no selectivity was observed between **1f** and **1g**.

The results of an electrochemical ring opening of styrene oxide in methanol apparently demonstrates usefulness of the electrolysis method (Table 3) compared with conventional chemical-acid catalyzed reactions.

These results demonstrate the potential of electrochemistry as a tool for efficient alcoholyses and hydrolyses of different classes of epoxides. High yield, ease of the work-up, and high regio, stereo and competitive selectivity can make this method a useful addition to the present methodologies in organic synthesis.

Experimental

The products were characterized by comparisons of their physical data (IR, NMR, and mass spectra) with those prepared according to procedures described in the literature. All of the yields refer to isolated products. Preparative electrolyses were conducted using a PAR model 170 electroanalyzer. Infrared spectra were recorded on Perkin–Elmer IR-157 G and Perkin–Elmer 781 spectrometers. NMR spectra were recorded on Hitachi (R-2413) 60 MHz or varian (XL-100) spectrophotometer. The mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. The purity determination of the substrates and reaction monitoring were accomplished by using TLC on silica-gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-8A instrument with a flame-ionization detector using a column of 15% Carbowax 20M Chromosorb-w acid washed 60—80 mesh. The chemicals were purchased from Fluka and Merck chemical companies. The products were separated and purified by different chromatography techniques.

Typical Procedure: Electrolyses of styrene oxide in methanol. A mixture of styrene oxide (0.6 g, 5 mmol) in methanol (50 mL) containing 0.2 M of sodium perchlorate (1 M=1 mol dm^{-3}) as an electrolyte was electrolyzed in a divided cell at a platinum anode and cathode at room temperature for 5 min either at constant potential of +1.1, volts or under constant-current conditions. The reaction was then stirred for an additional 10 min while being monitored by GLC. The amount of consumed electricity was found to be 0.0026 F mol^{-1}. The solvent was removed under a vacuum. After water was added (25 mL), the mixture was extracted with ether (3×50 mL) and washed with a 5% aqueous solution of sodium hydrogencarbonate. The organic solution was dried ($MgSO_4$). Evaporation of the solvent, followed by vacuum distillation or chromatography on a short column of silica-gel, gave pure 2-phenyl-2-methoxyethanol as a colorless liquid (0.64 g. 98%, bp 60 °C/0.2 mm, lit,[15] 75 °C/0.7 mm). It's 1-naphthylurethane was obtained as fine colorless needles (mp 122—123 °C, lit,[15] mp 120 °C).

Table 3. A Comparison between Electrochemical and Chemical Acid-Catalyzed Reaction of Styrene Oxide (**1a**) in Methanol and at Room Temperature

Acid[a)]	Time	Product **2a** (%)	Acid	Time h	Product **2a** (%)
Electrolysis	15 min	98	Cl_3CCOOH	2	80
CH_3COOH	18 h	70	60% $HClO_4$aq	18	85
HCOOH	18 h	80	$BF_3{\cdot}Et_2O$	1	85

a) The reaction of styrene oxide was performed with 1 molar equivalent of each acid.

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