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## Highly Regioselective Electrochemical Epoxide Ring Opening Reactions by Alkyl Halides Using Sacrificial Anodes and Stainless Steel Cathode

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Electrochemical technique has been known as a powerful tool in generating many active species which may not be formed by conventional chemical methods. As a matter of fact, a wide variety of organic chemical transformations can be carried out rapidly and in good yields, using relatively simple equipment, with the added advantage of avoiding hazardous, toxic reagent or byproduct. Especially, electrochemical process by a sacrificial anode in order to permit the formation of carbanions in undivided cell provided an extremely convenient methodology. That is, normally carbanions generated at the cathode would migrate to the anode and be destroyed by oxidation there. However, if the anode is made of an electropositive metal, the anode reaction becomes oxidation of the metal anode itself. These metal ions formed at the anode presumably coordinate with the carbanions generated electrochemically at the cathode to afford organometallic species, which react more readily with added electrophile than the free carbanion. In order to apply this view to the synthetic purposes, we decided to utilize this sacrificial anode for electrochemical epoxide ring opening reactions by alkyl halides. The electrochemical results of our study are summarized in Table 1 along with comparative data for Grignard reactions of the corresponding epoxides.

In our electrochemical epoxide ring opening reactions with alkyl halides, stainless steel as working electrode, and copper, magnesium, aluminium and zinc as sacrificial anodes were employed. And tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) as a supporting electrolyte and N,N-dimethylformamide (DMF) as a solvent were used in these electrochemical reactions. The amount of epoxide ring opening products was measured as current yields which were the ratio of the actual amount consumed to theoretical amount of electricity required to effect a given reaction. And re-

gioselectivity of electrochemical reaction products was compared with Grignard reaction products.

As would be anticipated for an S<sub>N</sub>2 process, electrochemical epoxide ring opening occurs at the less substituted position. In the case of 1,2-epoxybutane with primary alkyl halide, such as 1-bromobutane, current yields were quite different to depend upon the sacrificial anodes but the regioselectivity of products was very high compared to those of Grignard reactions. Furthermore, as the alkyl halides become more bulkier, the regioselectivity was increased dramatically in electrochemical processes. Especially in the case of tertiary alkyl halide such as 2-bromo-2-methylpropane, the regioselectivity was shown to be 100%. It was very surprising results compared with Grignard reaction which gave the corresponding products in a ratio of 89:11. However, the electrochemical reaction of benzylchloride with 1,2-epoxybutane afforded the low regioselectivity like Grignard reaction. In the case of styrene oxide with alkyl halides, all electrochemical reactions gave the sole product in a ratio of 100:0 while Grignard reaction afforded the two products in considerably low regioselectivity.

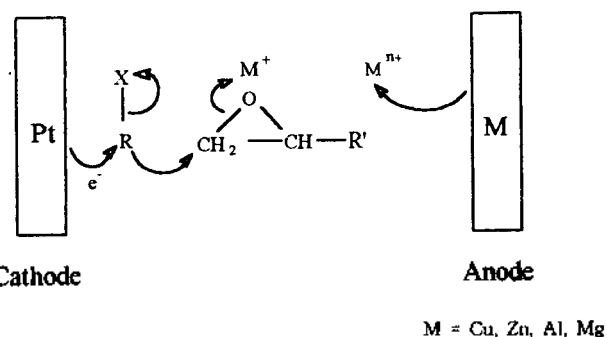
Although we do not have the reasonable explanation for these high regioselectivities of this electrochemical epoxide ring opening reactions, we could explain as follows. First of all, metal cations are generated at the sacrificial anode, and coordinate to the electron rich site of epoxides. These epoxides, being positively charged by metal cation, will move toward the cathode. At the same time, the carbanions are generated by the alkyl halides on the cathode surface. And these two charged species are arranged in order of carbanions and epoxides on the bulky cathode surface to have the less steric hindrance each other, and they react rapidly before they are diffused uniformly into the solution as shown in Scheme 1.

**Table 1.** Electrochemical ring opening reaction of epoxides with alkyl halides in DMF<sup>a</sup>

Epoxide	Alkylhalide	Anode	Current yield <sup>b</sup> (%)	Product
				A : B
1,2-epoxybutane	1-bromobutane	Cu	38	90:10
		Al	24	92:8
		Zn	36	87:13
		Mg	46	88:12
		Mg <sup>d</sup>	70 <sup>c</sup>	65:35
1,2-epoxybutane	2-bromobutane	Cu	38	90:0
		Al	24	92:8
		Zn	36	87:1
		Mg	46	88:12
		Mg <sup>d</sup>	64 <sup>c</sup>	69:31
1,2-epoxybutane	2-bromo-2-methylpropane	Cu	44	100:0
		Al	25	100:0
		Zn	37	100:0
		Mg	28	100:0
		Mg <sup>d</sup>	57 <sup>c</sup>	89:11
1,2-epoxybutane	benzyl chloride	Cu	59	65:35
		Al	37	60:40
		Zn	31	70:30
		Mg	43	52:48
		Mg <sup>d</sup>	78 <sup>c</sup>	58:42
styrene oxide	1-bromobutane	Cu	48	100:0
		Al	39	100:0
		Zn	29	100:0
		Mg	33	100:0
		Mg <sup>d</sup>	65 <sup>c</sup>	76:24
styrene oxide	2-bromobutane	Cu	39	100:0
		Al	42	100:0
		Zn	28	100:0
		Mg	29	100:0
		Mg <sup>d</sup>	70 <sup>c</sup>	71:29
styrene oxide	2-bromo-2-methylpropane	Cu	39	100:0
		Al	42	100:0
		Zn	28	100:0
		Mg	29	100:0
		Mg <sup>d</sup>	50 <sup>c</sup>	90:10
styrene oxide	iodomethane	Cu	50	100:0
		Al	68	100:0
		Zn	34	100:0
		Mg	28	100:0
		Mg <sup>d</sup>	75 <sup>c</sup>	53:47

<sup>a</sup>The electrochemical reactions were carried out at  $-3.2$  V vs SCE in undivided cell. <sup>b</sup>Current yields were determined by the ratio of the actual amount consumed to theoretical amount of electricity required to effect a given reaction. <sup>c</sup>A and B refer to more highly substituted alcohol and less highly substituted alcohol respectively. <sup>d</sup>The reaction was carried out by Grignard reaction process at r.t. in THF. <sup>e</sup>chemical yields.

And we tried to find a correlation between the current yields or regioselectivities, and the selection of sacrificial anodes. However, so far we could not find it in all tested electrochemical epoxide ring opening reactions.

**Scheme 1.**

Overall, our electrochemical epoxide ring opening reactions provide more convenient, safe, and regioselective methodology than the conventional organometallic reactions, such as Grignard reaction which is difficult to prepare and gives a low regioselectivity.

The following procedure for the electrochemical ring opening of 1,2-epoxybutane by 1-bromobutane is representative. The glass cell (50 mL) equipped with two electrodes was flushed with nitrogen. A solution of 1.72 mL of 1,2-epoxybutane (20.0 mmol), 0.22 mL of 1-bromobutane (2.0 mmol) and 0.33 g of tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>, 1.0 mmol) in DMF (30 mL) was placed in the cell equipped with cathode (stainless steel) and anode (Cu, Mg, Zn, or Al). The reaction was carried out at room temperature controlling the cathode potential at  $-3.2$  V vs SCE (saturated calomel electrode). When 2 mF (193 C) of electricity has passed, the reaction mixture was hydrolyzed with 10 mL 2 N HCl (10 mL) and diethyl ether (10 mL). The aqueous layer was saturated with sodium chloride and organic layer was subjected to GLC analysis on Chromosorb-WHP (10% SE-30, 10% Carbowax, 2 m, 1/8 inch column) indicating 19% of 3-octanol and 2-ethylhexanol in a ratio of 90:10. And 38% of current yield in Cu anode was calculated by the ratio of GLC yield to the electricity passed during the reaction.

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