

## Selective Reduction of the Carbon-Bromine Bond in Bromo Epoxides

N. Bhuvanewari, C.S. Venkatachalam\* and K.K. Balasubramanian\*

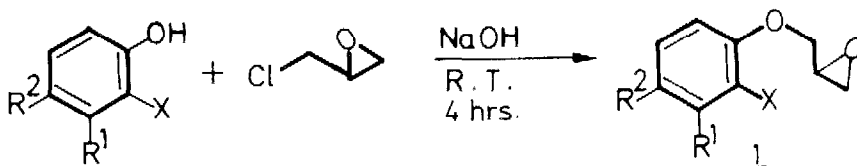
Department of Chemistry  
Indian Institute of Technology  
Madras - 600 036, INDIA

**ABSTRACT :** The controlled-potential electrolysis of various substituted bromo epoxides in acetonitrile at a mercury pool electrode led to selective reduction of the carbon-bromine bond affording the respective epoxide products in 80-90% yield.

Recently, we reported a selective cathodic reduction of carbon-chlorine bond in  $\beta$ -chlorovinylimines<sup>1</sup>. In continuation of our work in this area, we were interested to explore the synthetic utility of electrochemical method for the selective reduction of the carbon-bromine bond in compounds containing both the carbon-bromine and epoxide groups. While the reverse selectivity could easily be achieved, till now there seems to be no convenient method for the above conversion. Reagents and conditions that are normally employed for bringing out the reduction of the carbon-bromine bond<sup>2</sup> are too vigorous for the epoxide group to survive.

In the present communication, we report an electrochemical method for the selective reduction of the carbon-bromine bond in various substituted epoxides (**1a-1e,2**) in anhydrous acetonitrile. A series of bromo epoxides (**1a-1e**) were prepared by stirring the appropriate phenol (10 mmol) with (chloromethyl)oxirane (15 mmol) in 10 mL aqueous sodium hydroxide (1.0 M) at room temperature for four hours (Scheme 1). All these bromoaryl epoxides were thoroughly characterised by spectral data.

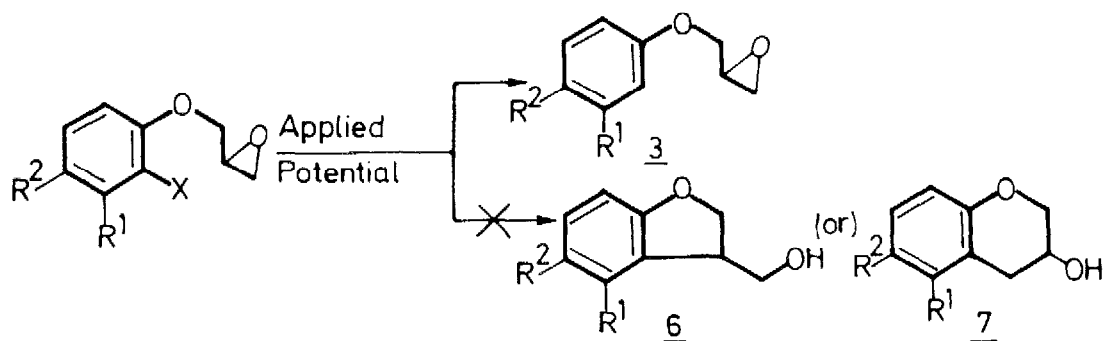
Scheme 1



A divided cell containing mercury pool as the working electrode and platinum foil as the anode was used for electrolysis. The electrolysis of various compounds

( $2 \times 10^{-2}$  M) was carried out at a constant potential of  $-2.25$  V vs. silver wire electrode in acetonitrile as solvent containing five equivalents of triethylamine and  $0.1$  M tetraethylammonium perchlorate as the supporting electrolyte (Scheme 2). Electrolysis was stopped when the current decreased to a minimum value. The catholyte solution was evaporated under reduced pressure to remove the solvent. The residue was repeatedly extracted with ether and the ether extract evaporated to yield a brown liquid which was finally purified by chromatographic techniques to afford epoxides **3a-3e**, which were characterised by spectral methods and structures confirmed by comparison with authentic samples prepared according to the procedure described above.

Scheme 2

TABLE 1<sup>#</sup>

Entry	S.No.	R <sup>1</sup>	R <sup>2</sup>	X	Yield (3) %
1.	<b>1a</b>	H	H	Br	85
2.	<b>1b</b>	H	CH <sub>3</sub>	Br	80
3.	<b>1c</b>	H	Cl	Br	88
4.	<b>1d</b>	H	Br	H	92
5.	<b>1e</b>	-CH=CH-CH=CH-		Br	82

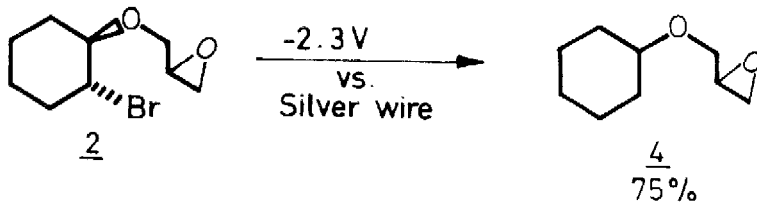
# Electrolysis was carried out at a potential of  $-2.25$  V for all the compounds from **1a-1e** using model 555B, AMEL, potentiostat.

It is worth mentioning here that a careful analysis of the crude product did not indicate the formation of any 1,2-dihydrobenzofuran-3-methanol **6** or 3-chromanol **7**, products which could arise by intramolecular opening of the epoxide by the carbanionic species formed by two-electron addition. Formation of these compounds

from **1a** in the presence of n-BuLi and  $\text{MgBr}_2/\text{n-BuLi}$  is known<sup>3</sup>.

In a similar manner, the electrolysis of [(2-bromocyclohexyloxy)methyl]oxirane **2** gave the corresponding debrominated product **4**, in 75% yield (Scheme 3).

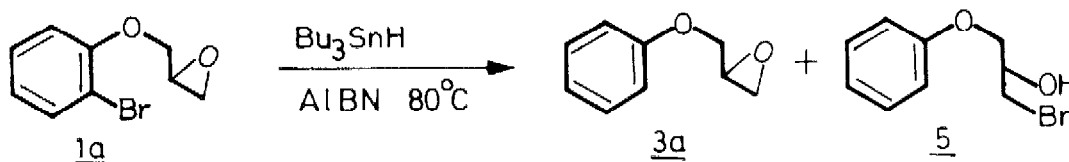
Scheme 3



The basic polarographic and cyclicvoltammetric studies of **1a**, for example, showed a single cathodic wave and peak respectively ( $E_{1/2} = -2.10$  V;  $E_{p,c} = -2.20$  V vs. silver wire electrode), which corresponds to a two-electron reduction. It is suggested that there is a protonation of the initially formed anion either by the solvent or supporting electrolyte or by traces of moisture present in the solvent<sup>4,5</sup>. The presence of triethylamine in the medium is highly essential, as in the absence of it, invariably a mixture of products is obtained.

Since an isolated epoxide group is known to be stable under tri-n-butyltin hydride - AIBN reaction conditions<sup>6</sup>, it was of interest to examine the behaviour of the bromo epoxide **1a** towards the above reagent. Refluxing a solution of **1a** in benzene (2mM) with one equivalent of tri-n-butyltin hydride in the presence of catalytic amount of AIBN for eight hours afforded a liquid in 80% yield which was found to be a 1:1 mixture of **3a** and **5** (Scheme 4).

Scheme 4



The lability of the epoxides under the above conditions highlights the synthetic potential of the cathodic reduction method described in this paper.

The electrochemical reduction of haloaliphatics and haloaromatics is well documented in the literature<sup>7-9</sup>. In contrast, the study of the reduction of epoxides has drawn a very little attention<sup>10</sup>. Recently, Torii et al have reported a novel synthetic route to aldols by indirect electroreductive cleavage of epoxy ketones<sup>11</sup>. Reduction of epoxyketo systems for the generation of hydroxy ketone in a steroidal

framework has also been effected<sup>12</sup>. The present work brings out yet another useful application of the electrochemical method in organic synthesis.

#### ACKNOWLEDGEMENTS

One of us (NB) is grateful to CSIR, India for a fellowship. We are thankful to Prof. G. Schröder and Dr. H. Röttele, University of Karlsruhe, Germany, Prof. T.R. Govindachari and Dr. T. Rajamannar, SSF, Madras, Dr. K. Nagarajan, Searle (India) Ltd., Bombay and RSIC, IIT, Madras for spectral data, Prof. T.R. Balasubramanian, Vivekananda College, Madras for gift of various chemicals. We also thank M/s. BAYER AG, Germany for ChemInform issues.

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(Received in UK 11 November 1991)