# Anodic Behaviour of Epoxides: Conditions for an Electron-transfer Chain Isomerisation induced by the Electrode

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The electrocatalytic isomerisation of epoxides is observed anodically in acetonitrile free from strong nucleophiles; the electrochemically induced isomerisation and the similar isomerisation caused by strong acids are compared.

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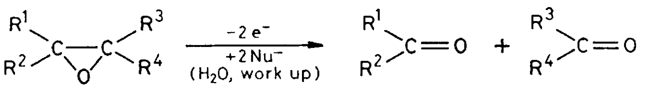
Epoxides are known to be electroactive both at the cathode[1,2] and at the anode.[3] At the anode[3] or in solution in the case of indirect oxidation,[2] it may be demonstrated that transient radical cations are decomposed rapidly by strong nucleophiles (*e.g.*, water present in acetonitrile) to lead to the corresponding carbonyl compounds (Scheme 1). Generally, the carbonyl derivatives produced are less easily oxidized than the substrate at the anode.

The aim of the present note is to show that the fate of the intermediate radical cation can be *dramatically changed* when the solvent is made sufficiently free of efficient nucleophiles. Such anodic experiments may be carried out either in super-dry acetonitrile[4] (in the presence of carefully activated alumina) or in methylene dichloride. Under these conditions, the amount of electricity consumed is very low (*ca.* 0.1 Faraday per mole) and the main product is the ketone (**4**) (assuming that $R^3$ is the fastest migrating group) resulting from the rearrangement of (**1**) (Scheme 2). Table 1 summarizes our results for the epoxides (**1**) ($R^1$—$R^4 \neq$ H, except for one substrate, in order to avoid a possibly fast deprotonation of the radical cation).

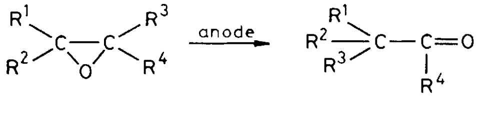
Similar results are obtained on addition strong acids; indeed, an excess of acid (such as perchloric or toluene-*p*-sulphonic acid) may isomerise (**1**) into (**4**) rapidly at room temperature in the dark.

However, if the amount of added strong acid is calculated on the basis of the amount of electricity consumed (assuming that the loss of 1 electron corresponds to 1 equivalent of acid), under the conditions in Table 1, the concentration of added acid appears to be too low to cause the isomerisation of (**1**) on the time scale of an electrolysis. In principle, the decomposition of (**1**) may be followed by cyclic voltammetry; for moderately slow sweep rates (50—100 mV/s), a net shift of the oxidation peak to more oxidative potentials is observed for the second and succeeding sweeps. This new oxidation peak is probably due to the ketone (for the phenyl substituted epoxides), and disturbs the observation of the electrocatalysis on a micro-anode.



(1) (2) (3)

**Scheme 1**



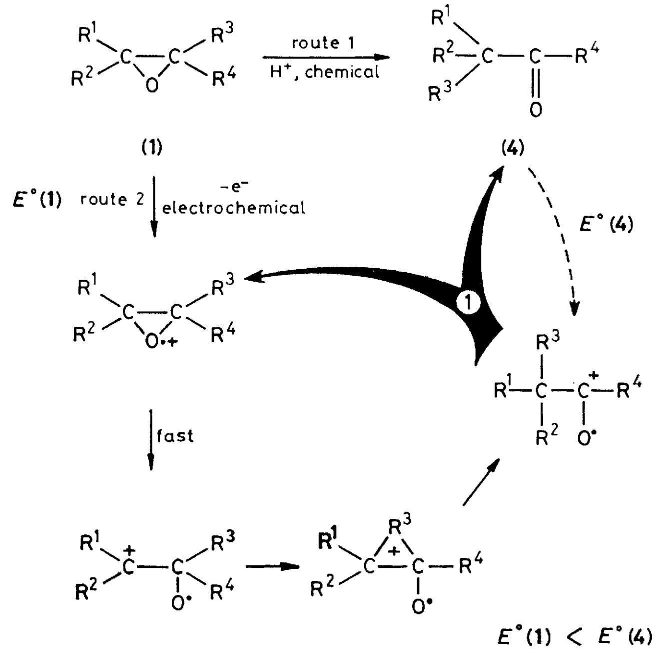
(1) (4)

**Scheme 2**

**Table 1.** Voltammetry and fixed-potential electrolysis of the epoxides (**1**) in poorly nucleophilic solvents.[a]

| Epoxide (**1**) | $E_p$/V[b] | $E_{ox}$/V[c] | Electrolyte[d] | Electricity consumed/ (Faraday mol$^{-1}$)[e] | Amount of (**1**)/ mmol | % Yield | |
|---|---|---|---|---|---|---|---|
| | | | | | | (**2**) | (**4**) |
| $R^1$—$R^4$ = Ph | +1.82 | +1.90 | A | 0.05 | 10 | 10 | 90 |
| $R^1$ = $R^3$ = Ph, $R^2$ = $R^4$ = Me | +1.90 | +1.95 | A | 0.05 | 1 | 3 | 97 |
| $R^1$—$R^4$ = Me | +2.15 | +2.50 | B | 0.02 | 12 | | 100 |
| $R^1$—$R^3$ = Me, $R^4$ = H | +2.40 | +2.50 | B | 0.025 | 200 | | 100[f] |
| $R^1R^3$ = -[CH$_2$]-, $R^2$ = $R^4$ = Me | +2.38 | +2.50 | A | 0.10 | 12 | | 30[g] |

[a] A divided cell was used. [b] Reference electrode Ag/Ag$^+$ (0.1 M); substrate concentration $5 \times 10^{-3}$ M. For $R^1$—$R^4$ = Et, $E_p$ = 1.95 V. [c] Working electrode platinum anode, area 10 cm$^2$. [d] A = LiClO$_4$ (0.1 M) in MeCN; B = Bu$_4$NClO$_4$ (0.1 M) in CH$_2$Cl$_2$. [e] The reaction stops with an electrolysis current of <5 mA. [f] MeCOPr$^i$. [g] CH$_2$[CH$_2$]$_3$CMeCOMe.



Scheme 3

Thus the addition of a proton and the loss of an electron may have a similar or identical effect in the rearrangement of epoxides; H$^+$ may have an oxidative effect and such properties were exemplified recently[5] in the anodic tetramerisation of benzylaziridines. In the same manner that a nucleophile can initiate $S_{RN}1$ reactions[6] by its possible reducing properties, H$^+$ may play a similar role as acceptor in oxidative chain processes. The electrocatalytic mechanism in Scheme 3 is proposed for isomerisation of epoxides. This mechanism is based on the assumption that the standard oxidation potential of the ketone is larger than that of the corresponding epoxide, this making the propagation of the chain feasible. This proposal appears reasonable since ketones are known to be difficult to oxidize anodically.

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