

Alkene Formation in the Cathodic Reduction of Oxalates

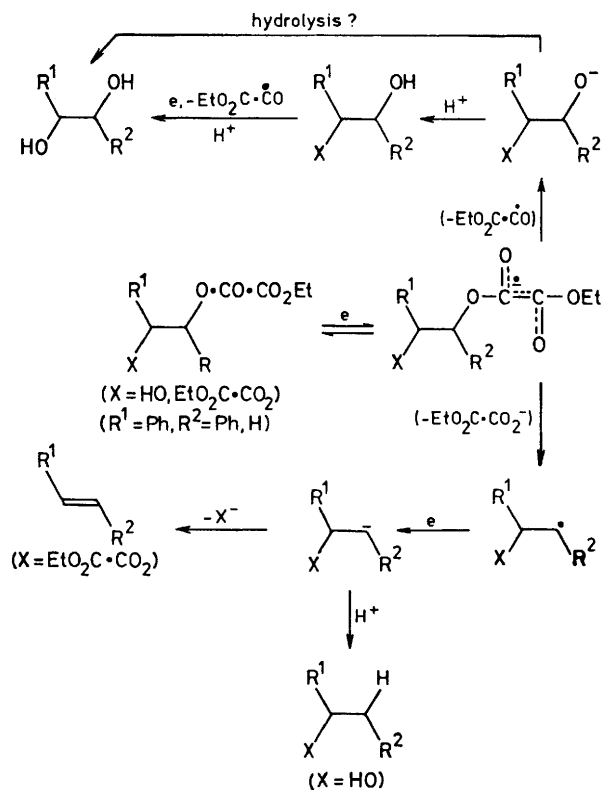
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Summary Oxalates undergo fragmentation and elimination upon cathodic reduction at relatively modest potentials and this method, when applied to vicinal dioxalates, is useful for alkene formation under mild conditions and, when applied to a mono-oxalate, allows selective cleavage of a hydroxy-group.

It has been observed¹ that in aprotic solution some oxalates (*e.g.* diethyl oxalate) reduce reversibly at moderately low potentials to give relatively stable radical-anions whereas others (*e.g.* diallyl and dibenzyl oxalates) reduce irreversibly. Recent work on cathodic cleavage and elimination reactions² which are of considerable interest for synthesis,

raises the previously unexplored possibility (Scheme) that where irreversible reduction of oxalates occurs it is a result of rapid fragmentation and/or elimination to olefinic products. Oxalates reduce in the region of -1.2 V (*vs.* Ag/AgI), *i.e.* much lower than for vicinal dibromides³



SCHEME

[-1 to -2 V (*vs.* S.C.E.)], vicinal diacetates^{2a} (*ca.* -1.8 V), or vicinal diols⁴ [> -2 V (*vs.* S.C.E.)] (S.C.E. = saturated calomel electrode). Cleavage of such vicinal functions is usually accompanied by rapid stepwise elimination^{2a} and at

substantial negative potentials olefinic products are further reduced. We report herein on experiments which use oxalate ester reduction as a method (a) for deoxygenation at potentials sufficiently low to preserve olefinic products and (b) as a method for selective removal of one of the vicinal hydroxy-groups.

The compounds studied and their reduction peak potentials, determined by cyclic voltammetry, are listed in Table 1. Controlled potential coulometry for reduction of oxalates (2) and (3) gave, in *NN*-dimethylformamide (DMF) solution, $n = 1$; in each case addition of acetic acid caused an increase to $n = 2$. The oxalates (1)–(3) showed quasi-reversible reduction at higher sweep speeds; the reverse oxidation peak for diethyl oxalate (1) was observable at 1 V s⁻¹ whereas for compounds (2) and (3) the reverse peak (at -1.10 V) became significant at 10 V s⁻¹ ($i_p^a/i_p^c = 0.3$ and 0.2 respectively). In the presence of acetic acid the reductions were irreversible at ≤ 100 V s⁻¹ with $n = 2$. Estimates of the lifetimes of the radical-anions of (1) and (3), generated cathodically, were made from the first-order decay of their e.s.r. spectra;† approximate $t_{1/2}$ values at *ca.* 20 °C are for (1) 1.5 s, and for (3) 0.7 s.

In contrast, the oxalates of vicinal diols gave irreversible reduction under protic and aprotic conditions at scan rates up to 100 V s⁻¹. Examination of the products of preparative-scale controlled-potential electrolysis (Table 2) reveals that, consistent with the hypothesis embodied in the Scheme, fragmentation and elimination lead to alkene products which survive further reduction. The formation of only *trans*-stilbene from either *meso*- or (\pm)-dioxalates implies stepwise conversion as shown in the Scheme. It also proved possible, using ethyl oxalyl chloride without a basic catalyst, to functionalise one of the vicinal hydroxy-groups [compound (4)]. In this case reductive elimination appears to be slow and a significant proportion of the product has only one oxygen function removed. It is conceivable that the diol products result from hydrolysis catalysed by basic conditions at the cathode, particularly for (4) where assistance from the neighbouring hydroxy-group is possible. However, such hydrolysis would not involve exclusive attack at one carbonyl function and it is known that more readily hydrolysed compounds, *e.g.* aryl boronates,⁵ survive similar reduction conditions.

TABLE 1. Reduction peak potentials (E_p^c).^a

Oxalate		$-E_p^c$ /V (<i>vs.</i> Ag/AgI)
EtO ₂ C•CO ₂ Et	(1)	1.30
PhCH ₂ O ₂ C•CO ₂ Et	(2)	1.26
		(1.36; $-E_p^a$, 1.10 V) ^b
PhCH ₂ O ₂ C•CO ₂ CH ₂ Ph	(3)	1.20
		(1.29; $-E_p^a$, 1.10 V) ^b
<i>meso</i> -HOCH(Ph)CH(Ph)O ₂ C•CO ₂ Et	(4)	1.27
<i>meso</i> -EtO ₂ C•CO ₂ CH(Ph)CH(Ph)O ₂ C•CO ₂ Et	(5)	1.20
(\pm)-EtO ₂ C•CO ₂ CH(Ph)CH(Ph)O ₂ C•CO ₂ Et	(6)	1.20
<i>meso</i> -PhO ₂ C•CO ₂ CH(Ph)CH(Ph)O ₂ C•CO ₂ Ph	(7)	0.97
PhO ₂ C•CO ₂ CH(Ph)CH ₂ O ₂ C•CO ₂ Ph	(8)	1.00

^a Substrates *ca.* 2×10^{-3} mol dm⁻³, Hg-coated Pt bead cathode, DMF–Bu₄Ni (0.1 M), scan rate 0.4 V s⁻¹. ^b Scan rate 10 V s⁻¹; E_p^a = anodic peak.

† E.s.r. spectroscopic measurements were made by Dr. U. Akbulut, Dr. K. D. Sales, and Mr. A. Oduwole.

TABLE 2. Products of controlled potential electrolysis.^a

Oxalate	$-E_{\text{red}}/V$ (vs. Ag/AgI)	Products (% yield) ^b
(4)	1.30 (1.1 F mol ⁻¹)	<i>meso</i> -HO.CH(Ph)CH(Ph).OH (31) HO.CH(Ph)CH ₂ Ph (11)
(5)	1.20 (2.0 F mol ⁻¹)	<i>trans</i> -PhCH:CHPh (23)
(6)	1.20 (2.0 F mol ⁻¹)	<i>trans</i> -PhCH:CHPh (75)
(7)	1.10 (1.6 F mol ⁻¹)	<i>trans</i> -PhCH:CHPh (45) <i>meso</i> -HO.CH(Ph)CH(Ph).OH (22)

^a Divided cell, Hg pool cathode, DMF-Bu₄NClO₄ (0.1 M).

^b Based on starting material, measured by ¹H n.m.r. spectroscopy.

Because of the low cathodic potential required the method should be useful for removal of hydroxy-groups in the presence of other reducible functions. The potentials required are uniformly in the region of -1.20 V and this offers the possibility of devising reaction conditions for easy operation at controlled current.

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