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ELECTRO-ORGANIC REACTIONS. PART 27. THE MECHANISM OF CATHODIC CLEAVAGE OF ACTIVATED ESTERS; OXALATES, SQUARATES AND OXAMATES

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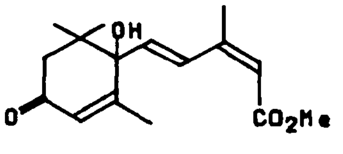
Abstract - Esters of oxalic acid, 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid), and oxamic acid, are reduced cathodically at modest potentials. In aprotic solvent, and on the cyclic voltammetric time scale, the esters are cleaved to the corresponding alkane. For oxalates, the mechanism of cathodic cleavage was investigated thoroughly by voltammetry, coulometry, and detailed product analysis. On the time scale of controlled potential electrolysis the rapid electrogenerated base-catalysed hydrolysis of the esters by adventitious water competes with cathodic cleavage. Similarly, rapid base-catalysed transesterification involving oxalates and added alcohols is observed which provides a practical method of reductively cleaving alcohols to alkanes by co-electrolysis of a mixture of alcohol and readily available oxalate (e.g. diethyloxalate). The leaving group in such cathodic fragmentation is the half-ester anion and the efficiency of reaction depends on the stability of the other, radical, fragment.

The direct reduction of alcohols to alkanes is difficult. In the attempted electrochemical cleavage of alcohols it has been established[1] that only at extreme cathodic potentials can hydroxyl be cleaved, from benzylic positions. Furthermore, in some cases (e.g. pinacols), cleavage of carbon-carbon bonds is the preferred reaction;[2] even when the hydroxyl group is part of a highly electro-active structure, such as the abscisic acid ester (1), the reduction product (2) retains the hydroxyl function.[3] The poor nucleofugality of the hydroxyl group is modified by its conversion into esters, e.g. tosylates,[4] methane sulphonates,[5] diethylphosphates,[6] and acetates.[7] Although such derivatisation allows efficient cathodic cleavage, the potentials required are still very negative and likely to cause reduction of other functional groups in polyfunctional systems. Voss and his co-workers[8] observed that oxalate esters were easily reduced in aprotic solution and that diallyl and dibenzyl oxalates underwent rapid chemical reactions following electron transfer. We have reported[9] on preliminary experiments which illustrated the use of oxalate esters as both electrophores and leaving groups in a reaction which showed promise as a useful low-potential method for the preparative scale cleavage of carbon-oxygen bonds. The mechanism of that reaction was not obvious and we describe herein experiments which resolve the mechanistic problem and extend the synthetic application of the method.



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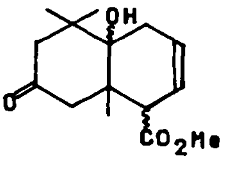


(2)

RESULTS AND DISCUSSION

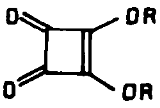
Earlier work[8,9] established that many oxalates showed quasi-reversible behaviour in cyclic voltammetric experiments and, through e.s.r. spectroscopy,[10] it was confirmed that for diethyloxalate (3b) and dibenzyloxalate (3g) the initial products of cathodic reduction were the corresponding radical anions. Their estimated lifetimes in DMF solution at 293K were, respectively, $t_{1/2}$ = 1.5s and 0.7s. The products of preparative-scale reduction were known[9] to be alcohols and alkanes; the overall possibilities for fragmentation are given in Scheme 1. In attempting to delineate the mechanism in greater detail a thorough voltammetric and coulometric examination of many oxalates of the general formulae (3) and (4) has been carried

$R^1O.COCO.OR^1$

(3)

$R^1R^2C(OX)C(OY)R^1R^3$

(4)



(5)

$R^1NHCO.CO_2R^2$

(6)

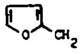
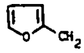
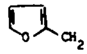
out. The principle of combining electrophore and leaving group has been applied to other esters, notably those of squaric acid (5) and oxamates (6). In several cases preparative electrolyses with careful product analysis has been necessary and the results have been accommodated in a consistent mechanistic rationalisation.

1. Single sweep cyclic voltammetry and controlled potential coulometry

(a) Oxalates of monohydric alcohols (3): These esters are reduced at relatively low potentials and in each case voltammetry was diffusion controlled as shown by linear plots of i_p *vs.* $v^{1/2}$. The benzylic esters are reduced at slightly lower potentials than the others (more anodic). Controlled potential coulometric experiments gave linear plots of i_p *vs* Q. The results of the cyclic voltammetric experiments are summarised in Table 1. Compounds (3a)-(3e) gave quasi-reversible reduction at a modest scan rate (0.235 Vs^{-1}) but for compounds (3f)-(3j) reduction was irreversible at < *ca* . 10-15 Vs^{-1}. Controlled potential coulometry showed that in each case, whether quasi-reversible or irreversible, n = 1; in several cases addition of proton donor caused a doubling of i_p at the first reduction potential.

The experiments involving compounds (3h)-(3j) are especially important and the relevant voltammogram for (3i) is given in Figure 1. In these cases three reduction peaks are observed and the third is quasi-reversible. For compounds (3h) and (3i) the third reduction peak was shown to be that for a product, 4-phenyltoluene. In comparison the cyclic voltammetry of 4-phenyltoluene (7.7 x 10^{-3} mol dm^{-3}, 0.35 Vs^{-1}) indicated quasi-reversible reduction at $E_{p,c}$ = -2.20V, $E_{p,a}$ = -2.07 V, and i_p^a/i_p^c = 0.9. Similarly, cyclic voltammetry of 4-phenylbenzyl chloride, which would be expected readily to cleave to 4-phenyltoluene, gave at 0.235 Vs^{-1} $E_{p,c}$ = -1.62 V (irrev.) and a quasi-reversible couple at $E_{p,c}$ = -2.20 V, $E_{p,a}$ = -2.07 V with i_p^a/i_p^c = 0.88. The quasi-reversible couple for (3h) and (3i) is therefore indicative of cleavage to 4-phenyltoluene.

Table 1. Oxalates (3): Cyclic Voltammetric Results[a]

Ester		Compound number	$-E_{p,c}$	$-E_{p,a}$	i_p^a/i_p^c
R^1	R^2				
Me	Me	3a	1.32	1.21	0.78
Et	Et	3b	1.39	1.24	0.76
Pr^i	Pr^i	3c	1.42	1.28	0.64
Bu^t	Bu^t	3d	1.52	1.35	0.55
Ph	Ph	3e	0.95	0.82	0.60
$PhCH_2$	Et	3f	1.34 (1.36	- 1.10	- 0.3)[b]
$PhCH_2$	$PhCH_2$	3g	1.23 (1.29	- 1.10	- 0.2)[b]
$4\text{-}Ph.C_6H_4CH_2$	Et	3h	1.26 1.84 (2.18	- - 2.04	- - 0.73)[c]
$4\text{-}Ph.C_6H_4CH_2$	$4\text{-}Ph.C_6H_4$	3i	1.18 1.86 (2.19	- - 2.03	- - 0.84)[c]
$PhCH{:}CHCH_2$	$PhCH{:}CHCH_2$	3j	1.18 1.85 (2.24	- - 2.03)[d]	- -
	Et	3k	1.25[b]		
		3l	1.20[b]		

[a] DMF-Bu_4NI; Hg coated Pt bead cathode; 0.235 Vs^{-1}; ester *ca.* 5 x 10^{-3} mol dm^{-3}; reference electrode Ag/AgI.

[b] Quasi-reversible (q.r.) at 10 Vs^{-1}; irreversible with i_p double in presence of HOAc.

[c] 1st and 2nd waves irrev. at <15 Vs^{-1}; 3rd wave q.r. at 15 Vs^{-1}.

[d] 1st and 2nd waves irrev., 3rd wave q.r.; i_p at 1st wave doubled in presence of quinol.

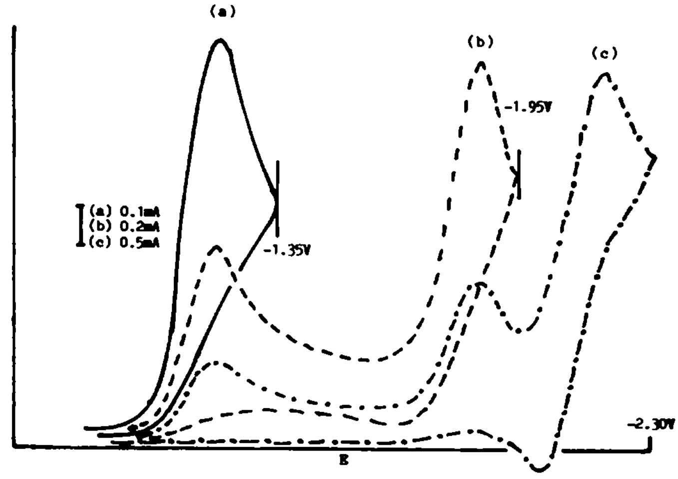


Figure 1. Cyclic voltammogram of di-(4-phenylbenzyl)oxalate (3i) with sweep reversal at: (a) -1.35V (*vs*. Ag/AgI); (b) -1.95V; (c) -2.30V. [Hg bead cathode, DMF-Bu_4NI (0.1M), 0.235 Vs^{-1}]

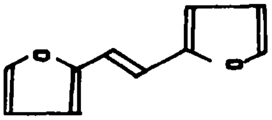
The second reduction peak, at $E_{p,c}$ = -1.86 V, common to (3h) and (3i), is probably due to reduction of $PhCH_2O.CO.CO_2^-$. There is further strong evidence that the half-ester anions are leaving groups in these cleavage reactions (section 3b). There is no indication that on the cyclic voltammetric time scale the alternative product, 4-phenylbenzyl alcohol, is formed although the alcohols are significant products in preparative scale experiments. 4-Phenylbenzyl alcohol is reduced at $E_{p,c}$ = -1.95 V under comparable conditions and there is no sign of such a reduction peak, e.g. in Figure 1.

(b) The role of rapid transesterification: The realisation that rapid transesterification was possibly important came from an attempted controlled potential electrolysis of 4-phenylbenzyl ethyl oxalate (3h) in dichloromethane solution containing Bu_4NBF_4, at -1.60 V. After passage of 0.25 F mol^{-1} di-(4-phenylbenzyl) oxalate (3i) was fortuitously precipitated. This observation raised the possibility of *in situ* formation of the required oxalates by reaction between alcohols and more readily available oxalates, e.g. the dialkyoxalates. Proof of such reaction was obtained by cyclic voltammetry and preparative scale electrolysis (see section 2a).

The characteristic cyclic voltammogram of diethyl oxalate (3b) was changed upon addition of 4-phenylbenzyl alcohol to the solution; the quasi-reversible couple at $E_{p,c}$ = -2.20 V, associated with 4-phenyltoluene, also appeared. At relatively high scan rates (> 7 Vs^{-1}) the diethyl oxalate quasi-reversible couple reappeared. On the time-scale of slow sweep cyclic voltammetry, therefore, it appears that formation of other oxalate esters (e.g. 3h and 3i) is rapid and that they cleave to the alkane. Similar changes in cyclic voltammograms were observed for the addition of 4-phenylbenzyl alcohol to solutions of the dialkyloxalates (3a) and (3c)-(3e).

(c) Oxalate of vicinal diols (4): The electrochemical behaviour of the diol dioxalates is significantly different from that of the esters of the monohydric alcohols. In particular: (i) reduction is exclusively irreversible; (ii) controlled potential coulometry indicates 2 F mol^{-1} reduction. As for compounds type (3) the reduction potentials for esters of benzylic alcohols are slightly lower than for the others (e.g. 4a and 4b). The cyclic voltammetric and controlled potential coulometric results are summarised in Table 2.

Cyclic voltammetry was also used to establish the products of reductive cleavage, results which were confirmed by preparative electrolysis. For compounds (4d) and (4e) the irreversible first reduction peak listed was followed by a quasi-reversible couple at $E_{p,c}$ = -1.72 V, $E_{p,a}$ = -1.59 V. Cyclic voltammetry of *trans*-stilbene under the same conditions gave a redox couple at $E_{p,c}$ = -1.72 V, $E_{p,a}$ = -1.60 V, i_p^a/i_p^c = 1.0. For compound (4g) the result was qualitatively similar with the quasi-reversible couple at $E_{p,c}$ = -1.78 V, $E_{p,a}$ = -1.70 V, i_p^a/i_p^c = 1.0. In comparison, 1,2-difurylethene (7) gives in cyclic voltammetry reversible reduction, $E_{p,c}$ = -1.82 V, $E_{p,a}$ = 1.76 V, i_p^a/i_p^c = 1.0.



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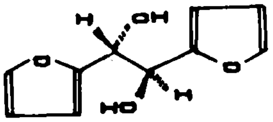


(8)

Furthermore, the production of alkene is directly related to the disappearance of starting material as followed by the diminution of current at the first peak; for 1,2-difurylethene its formation was shown in a controlled potential electrolysis to be linearly related to the disappearance of starting material.

Table 2. Oxalates (4): Cyclic Voltammetric and Coulometric Results[a]

	Ester ($R^1R^2C(OX)C(OY)R^1R^3$)						
R^1	R^2	R^3	X	Y	Compound number	$-E_{p,c}$	n
H	Me	Me	$OC.CO_2Et$	$OC.CO_2Et$	4a[b]	1.37	1.5 (1.7)[c]
Me	Me	Me	$OC.CO_2Et$	$OC.CO_2Et$	4b	1.40[d]	-
H	Ph	Ph	$OC.CO_2Et$	H	4c (meso)	1.27	1.1
H	Ph	Ph	$OC.CO_2Et$	$OC.CO_2Et$	4d (meso)	1.20[e]	2.0
					(±)	1.20[e]	2.0
H	Ph	Ph	$OC.CO_2Ph$	$OC.CO_2Ph$	4e (meso)	0.97[e]	1.6
H	Ph	H	$OC.CO_2Ph$	$OC.CO_2Ph$	4f	1.00	1.6
H			$OC.CO_2Et$	$OC.CO_2Et$	4g	1.18[e]	2.0

[a] DMF-Bu_4NI (0.1 M); substrate 2-5 x 10^{-3} mol dm^{-3}; v = 0.3 - 0.4 Vs^{-1}; Hg coated Pt bead cathode; reference electrode, Ag/AgI.

[b] Mixture of meso and (±) isomers

[c] In presence of quinol (4 equivalents)

[d] In MeCN-Bu_4NI (0.1 M)

[e] Redox couple for corresponding alkene also observed, see text.

The formation of oxalate esters of diols through rapid transesterification was proved by cyclic voltammetric experiments similar to those described in section 1b. In a typical experiment, addition of meso- or (±)-1,2-diphenylethan-1,2-diol, (which is not itself reducible at < -2.30 V), to the electrolyte containing diethyloxalate (3b) caused the quasi-reversible couple at -1.37 V to become irreversible with the concomitant appearance of the quasi-reversible reduction couple for stilbene at $E_{b,c}$ = -1.72 V, $E_{p,a}$ = -1.59 V. Similar behaviour was observed for cyclic voltammetry of mixtures of diethyloxalate and 1,2-di-p-methoxyphenylethan-1,2-diol; in each case the quasi-reversible peak for diethyloxalate reduction was restored at > 7 Vs^{-1}. The furan analogue (meso-1,2-difurylethan-1,2-diol (8)) was shown by the same method to participate in rapid transesterification with the oxalates (3a)-(3d), with production of (7).

(d) Esters of squaric acid (5): Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) is a strong acid ($pK_a(1)$ = 1, $pK_a(2)$ = 2.2)[11] because of stabilisation of the anion and dianion by extensive delocalisation. The same factor should cause the anion to be a good anionic leaving group. Furthermore, the adjacent carbonyl functions should confer ease of reduction upon its esters, by analogy with oxalates.

Cyclic voltammetric experiments (Table 3) confirm that the squarate esters are easily reduced, and in the case of (5e) there is good evidence for cleavage to 4-phenyltoluene

(Table 3, footnote f). The acid itself (5a) is even more readily reduced; *in situ* neutralisation with triethylamine revealed that the anions are not easily reduced.

Table 3. Squarates (5). Cyclic Voltammetric Results[a]

Ester (R)	Compound number	$-E_{p,c}$
H	5a	1.18[b]
Me	5b	1.48[c]
Et	5c	1.50[c]
$PhCH_2$	5d	1.65[c,d]
$4\text{-}Ph.C_6H_4CH_2$	5e	1.42[e] 1.92 2.22[f]

[a] As for Tables 1 and 2.

[b] Irreversible, addition of Et_3N eliminated reduction peak.

[c] No re-oxidation observed at up to 100 Vs^{-1}.

[d] Controlled potential coulometry gave n = 0.83, increasing to n = 1.30 in presence of quinol (2x).

[e] n = 0.86, increasing to n = 1.20 in presence of quinol.

[f] Quasi-reversible, $E_{p,a}$ = -2.07 V, i^a_p/i^c_p = 0.88

(e) Oxamates (6): For comparison with the oxalates two oxamates, ethyl oxamate ($EtO_2C.CONH_2$, (6a)) and benzyl-N-phenyloxamate ($PhCH_2O_2C.CONHPh$, (6b)) were examined by cyclic voltammetry. In each case irreversible reduction was observed at <100 Vs^{-1}; under the conditions described for Tables 1-3 $E_{p,c}$ for (6a) was -1.63 and for (6b), -1.29 V. Controlled potential coulometry gave n = 1; addition of hydrofuroin (8) to the ethyl oxamate solution gave cyclic voltammetry characteristic of rapid transesterification and cleavage to (7) (*cf.* section 1c).

2. Preparative scale controlled potential electrolyses

For the purpose of establishing mechanism only a representative selection of preparative-scale experiments will be described. Synthetically useful aspects of these reactions will be dealt with in subsequent papers.

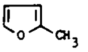
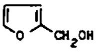
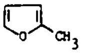
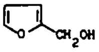
(a) The electrolysis of pre-formed esters: It is only for the vicinal, benzylic, diesters (4d) that preparative scale reduction gives useful conversion; in this case good yields of *trans*-stilbene were obtained from both diastereoisomers. This is compelling evidence for a stepwise reductive elimination, a point which will be discussed later.

Although alkanes are obtained in low yields from the other esters, (see Table 4), the corresponding alcohol is always a prominent product. This contrasts with the indications by cyclic voltammetry that, e.g. for esters (3h) and (5e), conversion into the alkane is efficient and no alcohol is detected. The difference arises from the different time scales of preparative *vs.* cyclic voltammetric experiments and from the relative wetness of solvents used for preparative electrolyses (see below).

The cyclic voltammetric evidence for rapid transesterification is reinforced by the preparative electrolysis of 4-phenylbenzyl ethyl oxalate (3h), during which the less soluble di-(4-phenylbenzyl)oxalate precipitated from the electrolyte.

Rapid transesterificaiton offers the possibility of re-conversion of the unwanted alcoho product into an oxalate ester.

le 4. Products from controlled potential electrolyses: preformed esters[a]

ter	$-E_{red}$	Products (% yield)[b]
alates		
	1.30^c	$PhCH_3$ (7); $PhCH_2OH$ (8)
	1.30^c	$PhCH_2OH$ (34)
	1.60^d	4-$PhC_6H_4CH_3$ (8); 4-$PhC_6H_4CH_2OH$ (9)
	1.60^e	 (14);  (40)
	1.60^e	 (13),  (35)
(meso)	1.20^c (2Fmol^{-1})	t-PhCH:CHPh (80)
(±)	1.20^c (2F mol^{-1})	t-PhCH:CHPh (75)
uarate		
	1.55^d	4-$PhC_6H_4CH_3$(32); 4-$PhC_6H_4CH_2OH$ (16)
amate		
	1.33^b	$PhCH_3$ (19); $PhCH_2OH$ (75)

Divided cells; reference Ag/AgI: 1 Fmol^{-1} except (4d)

By g.l.c. analysis, or ^1H n.m.r. spectroscopy with internal standard

Hg cathode; DMF-Bu_4NClO_4 (0.1 M)

Hg cathode; CH_2Cl_2-Bu_4NBF_4 (0.2 M)

Pb cathode; CH_2Cl_2-Bu_4NBF_4 (0.2 M)

Hg cathode; CH_2Cl_2-Bu_4NI (0.1 M)

Table 5. Preparative-scale electrolysis with in situ transesterification

$$R^1OH + R^2O_2C.CO_2R^2 \longrightarrow \longrightarrow R^1H + R^2O_2C.CO_2^-$$

Entry	R^2	R^1	$-E_{red}$	Products (% yield)
1.	Et	$PhCH_2$	1.60^c	$PhCH_3$ (73); $PhCH_2OH$ (20)[b]
2.	Et	4-Ph.C_6H_4.CH_2	1.60^d	4-Ph.C_6H_4.CH_3 (63)[e]
3.	Et	Ph_2CH	1.60^c	Ph_2CH_2 (70)[e]
4.	Et	Ph_2CH	1.60^f	Ph_2CH_2 (70)[e]
5.	Et	Ph_2CH	1.60^g	Ph_2CHOH (97)[e]
6.	Et	4-Ph.C_6H_4.$CH_2CH_2CH_2$	1.55^h	4-Ph.C_6H_4.$CH_2CH_2CH_2OH$ (96
7.	Me	Ph_2CH	1.55^h	Ph_2CH_2 (68)[e]
8.	Pr^i	Ph_2CH	1.65^h	Ph_2CH_2 (72)[e]
9.	Bu^t	Ph_2CH	1.75^h	Ph_2CH_2 (51)[e]
10.	Ph	Ph_2CH	1.40^h	Ph_2CH_2 (79)[e]
11.	Et	meso-PhCHCHPh	1.55^i	t-PhCH:CHPh (46)[e] $PhCH_2CH_2Ph$ (9)

[a] Divided cell; reference Ag/AgI; 2x excess of $R^2O_2C.CO_2R^2$; ca. 1.1-1.2 F mol^{-1} based on $R^2O_2C.CO_2R^2$

[b] G.l.c. analysis.

[c] Pb cathode; DMF-Bu_4NI (0.1 M)

[e] Isolated yield

[f] Carbon cathode; MeCN-Bu_4NBr (0.1 M)

[g] As for c, but with 5% w/v H_2O

[h] Pb cathode; MeCN-Bu_4NBr (0.1 M).

[i] As for h, but 3X excess of $EtO_2C.CO_2Et$

(b) Electrolyses via transesterification: The results collected in Table 5 show that efficient conversion of benzylic alcohols into the corresponding hydrocarbons is achieved by co-electrolysis of the readily available dialkyl and diphenyloxalates with alcohol. There are two experiments (entries 5 and 6) in which alkane is not obtained; in one case water (5% w/v) was deliberately added to the electrolyte and in the other a non-benzylic alcohol (p-biphenyl-3-propanol) was used. The mechanistic inference is that rapid hydrolysis of the oxalate can compete with transesterification and that stabilisation of the leaving group (benzylic radical?) is important.

3. Miscellaneous experiments; tests for evolution of CO_2 and CO, and the nature of the leaving group

(a) CO_2 and CO evolution: Should the oxalate ester radical-anions cleave to give either $RO_2C.CO_2^{\cdot}$, (by loss of R^- and ^-OR respectively), then rapid decarboxylation and decarbonylation would be expected.[12] These possibilities were excluded by the attempted detection of CO_2 and CO in a nitrogen stream passing through an electrolysing solution of diethyl oxalate. None was detected.

(b) The leaving group: It is conceivable that should $RO_2C.CO^{\cdot}$ be a product of radical-anion cleavage that it would react by hydrogen abstraction rather than by decarbonylation.[13] This was shown not to be the case by g.l.c. analysis of the products of electrolysis of diethyl oxalate; direct injection of a portion of the electrolyte, and comparison with authentic samples, showed that no detectable $EtO_2C.CHO$ was formed, whereas EtOH was.

The most convincing evidence for the nature of the leaving group was obtained by the preparation of $Bu_4NO_2C.CO_2Et$ (by phase-transfer exchange between $EtO_2C.CO_2K$ and Bu_4NBr) and a comparison of its ^1H n.m.r. and i.r. spectroscopic properties with the residue following electrolysis of diethyloxalate or co-electrolysis of Ph_2CHOH and diethyloxalate. In each case the ethyl group CH_2 signal was centred at δ_{CDCl_3}, 4.20 ppm, cf. δ4.38 in diethyloxalate Characteristic $\nu_{C=O}$ absorption was also observed at 1720 and 1630 cm^{-1} cf. 1740 cm^{-1} for diethyloxalate.

Finally, the products of complete electrolysis of diethyloxalate, (believed according to ^1H n.m.r. and i.r. spectroscopy, to contain $Bu_4NO_2C.CO_2Et$), were hydrolysed with 2N NaOH solution. Subsequent treatment with $CaCl_2$ gave a precipitate of calcium oxalate corresponding to 60% of the diethyloxalate electrolysed. Monoethyl potassium oxalate gave no precipitate with $CaCl_2$ under comparable conditions.

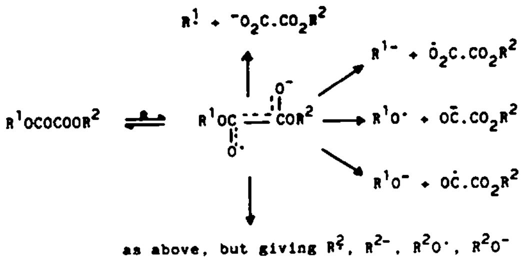
4. The Mechanism

The experimental observations to be accommodated are: (a) cleavage to alkane is efficient only for benzylic systems; (b) 1 F mol^{-1} is consumed; (c) vicinal diesters give reductive elimination wtih 2 F mol^{-1} reaction; (d) in preparative scale electrolyses in reagent grade solvents hydrolysis competes with cleavage - even for electrolysis with transesterification, addition of only 5% w/v H_2O causes hydrolysis to predominate; (e) no CO or CO_2 is evolved; and (f) the leaving group in the cleavage step is the half ester anion, $RO_2C.CO_2^-$. These facts are accommodated in the mechanism given in Scheme 2.

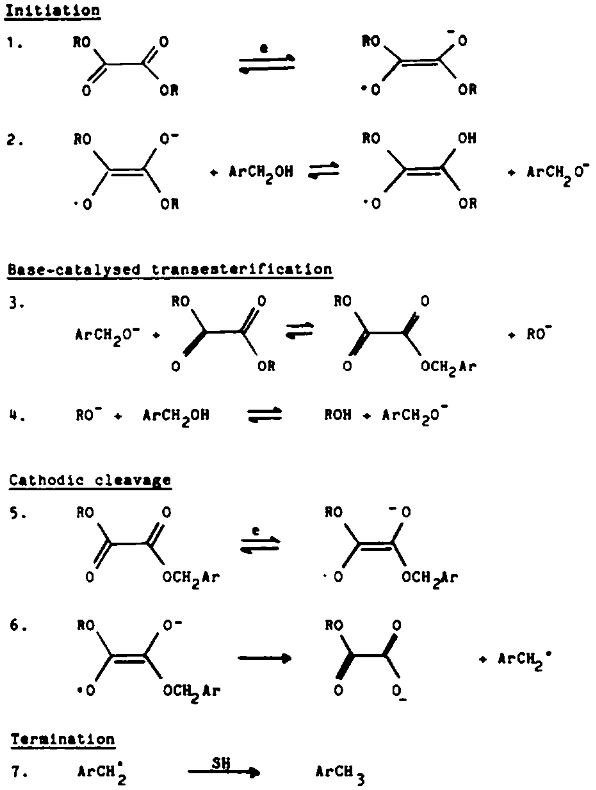
The crucial dependence on stabilisation of the departing radical has good precedence[12] in thermolytic reactions; diphenyloxalate is stable at up to 350°C whereas the corresponding benzhydryl oxalate decomposes readily at 200°C to give products derived from the benzhydryl radical. The fate of the radical is probably hydrogen abstraction (step 7) - further reduction and protonation would involve 2 F mol^{-1} reduction.

The rapid transesterification and hydrolysis reactions are also to be expected. During electrolysis the cathode compartment becomes progressively more basic; transesterification is therefore catalysed as described in Scheme 2 with steps 1 and 2 being initiation reactions consuming little current. Alkaline hydrolysis will occur either during aqueous work-up or during electrolysis through reaction with adventitious water. The leaving group, $RO_2C.CO_2^-$, will survive such conditions. For hydrolysis in aqueous alkali, at 25°C, relative rates[14] are: CH_3CO_2Me (1.0); $Me_2C.CO_2Me$ (1.7×10^5); $Me_2C.CO_2^-$ (8.4).

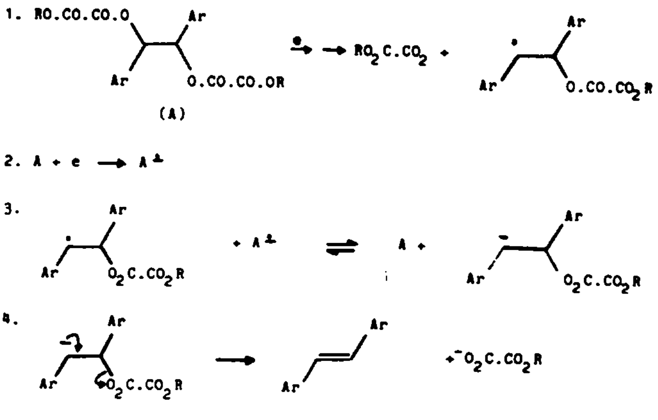
The reductive elimination of vicinal dioxalates, either pre-formed or formed *in situ* by transesterification, probably proceeds according to Scheme 3. In the light of recent mechanistic work on cleavage reactions[15] a homogeneous second electron transfer is suggested, although ECE reaction is also possible. The stepwise nature of the reaction is supported by the identical behaviour of *meso* and (±) diastereoisomers - a concerted process would favour formation of *trans*-stilbene from the *meso* isomer and *cis*-stilbene from the (±) isomer.



Scheme 1



Scheme 2



Scheme 3

EXPERIMENTAL

Oxalates (3); vicinal-di-oxalates (4); squarates (5)

Oxalates. Oxalyl chloride, ethyl oxalyl chloride, or phenyl oxalyl chloride, as appropriate, were added slowly at room temperature to an equivalent amount of the alcohol and pyridine, dissolved in ether. Dry, pure, materials were essential for efficient reaction. The mixture was heated under reflux for ca. 12h, except for the preparations of (3k), (3l) and (4g) where reaction at room temperature sufficed. The precipitate of pyridinium hydrochloride was removed, the filtrate washed (aq. $NaHCO_3$, H_2O), dried ($MgSO_4$), and the solvent removed. The esters were purified by distillation of recrystallisation (EtOH or C_6H_6). Yields were in the 60-90% range.

Squarates. These were prepared by reaction between disilver squarate[16] and the appropriate acid chloride, in dry ether. Reaction typically took two days at room temperature. After removal of silver chloride and solvent, the crude products were purified by recrystallisation [EtOAc or petrol (b.p. 40-60°)]. Compound (5e) was purified by column chromatography [silica, petrol (b.p. 40-60°)] to remove unreacted 4-phenylbenzoyl chloride and 4-phenylbenzyl alcohol.

Physical data relating to new compounds are collected in Table 6.

Electrochemical Experiments. Solvents, electrolytes, apparatus, and methods were as described in earlier papers in the series. Conditions for the experiments are given as footnotes to the relevant Tables.

Ethyl tetrabutylammonium oxalate was prepared by continous extraction with dichloromethane of an aqueous solution of ethyl potassium oxalate and tetra-n-butylammonium bromide. The dichloromethane solution was dried ($MgSO_4$) and solvent removed to give a viscous liquid; δ 4.2 ppm (q); ν, 1720, 1630 cm^{-1}.

Tests for CO_2 and CO formation were carried out by electrolysing diethyl oxalate in a closed cell and analysing the emerging stream of nitrogen either directly by bubbling through barium hydroxide solution (for CO_2) or by similarly testing for CO_2 after passing the gas stream over I_2O_5 heated at 145°C. Carbon monoxide is oxidised to CO_2 under these conditions and control experiments showed that CO or CO_2 formed during electrolysis would easily be detected.

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Table 6. Oxalates and Squarates

Compound	m.p. (b.p.)	Spectroscopic and analytical data
3c	(78°C/13 mm)	^{1}H n.m.r.: δ1.36 [12H, d, J7Hz, OC.OCH(CH$_3$)$_2$], 5.06 [h, 2H, J7Hz, OCOCH(CH$_3$)$_2$]; ν_{max}, 1738, 1760 cm^{-1}; m/z 174 (M$^+$, 32%), 159 (m-CH$_3$, 93%)
3d	70-71°C	δ1.58 [18H, s, OC.OC(CH$_3$)$_3$]; ν, 1740, 1760 cm^{-1}; m/z (M-Bu^{t}O$_2$C.CO$_2$, 100%)
3e	138-140°C	δ7.20 [10H, s, ArH]; ν, 1755, 740, 688 cm^{-1}; m/z, 242 (M$^+$, 100%), 214 (M-CO, 93%), 170 (M-CO-CO$_2$, 23%)
3f	(96-98°C/0.4 mm)	δ1.31 (3H, t, J7Hz, CO$_2$CH$_2$CH$_3$), 4.33 (2H, q, J7Hz, CO$_2$CH$_2$CH$_3$), 6.24 (2H, s, PhCH$_2$O$_2$C), 7.2-7.4 (5H, m, ArH); ν, 1775, 1750, 1310, 1185, 1140, 700 cm^{-1}
3h	89-90°C	(Found: C, 71.63; H, 5.74%; C$_{17}$H$_{16}$O$_4$ requires C. 71.82; H, 5.68%); δ1.35 (3H, t, J7Hz, CO$_2$CH$_2$CH$_3$), 4.35 (2H, q, J7Hz, CO$_2$CH$_2$CH$_3$), 5.36 (2H, s, ArCH$_2$), 7.33-7.73 (9H, m, ArH); m/z 284 (M$^+$, 119.4%, 183 (m-OC.CO$_2$Et; 14%), 167 (m-EtO$_2$C.CO$_2$, 100%; ν, 1760, 760, 700 cm^{-1}
3i	201-203°C	(Found: C, 79.5%; H, 5.29%; C$_{28}$H$_{22}$O$_4$ requires C, 79.60; H, 5.29%);δ5.38 (4H, s, ArCH$_2$), 7.33-7.48 (18H, m, ArH); m/z 422 (M$^+$, 16%), 183 (m-ArCH$_2$O$_2$C.CO, 9%), 167 (m-ArCH$_2$O$_2$C.CO$_2$ 100%); ν, 1755, 760, 725, 700 cm^{-1}.
3j	102-103°C	δ4.92 (4H, d, J6Hz, HC:CHCH$_2$OCO), 6.10-6.48 (1H, m, HC:CHCH$_2$O.CO), 6.77 (1H, d, J16Hz, PhCH:CH), 7.23-7.48 (10H, m, ArH); ν, 1760, 1740, 750, 700 cm^{-1}
3k	128°C/0.5 mm	(Found: C, 53.08; H, 4.78%; C$_9$H$_{10}$O$_5$ requires C, 54.55; H, 5.05%); δ1.25 (3H, t, J7Hz, CO$_2$CH$_2$CH$_3$), 4.35 (2H, q, J7Hz, CO$_2$CH$_2$CH$_3$), 5.30 (2H, s, ArCH$_2$O$_2$C), 6.24-6.58 (2H, m, ArH), 7.30-7.50 (1H, m, ArH); m/z 198 (M$^+$, 24%), 97 (m-EtO$_2$C.CO, 19%), 81 (M-EtO$_2$C.CO$_2$).100%; ν, 1765, 1740, 1015, 920, 883, 820 cm^{-1}
3l	61-62°C	δ5.23 (4H, s, ArCH$_2$O$_2$C), 6.30-6.55 (4H, m, ArH), 7.40-7.48 (2H, m, ArH); m/z 250 (M$^+$, 7%), 81 (M-ArCH$_2$O$_2$C.CO$_2$, 100%); ν, 1748, 1012, 920 882, 821 cm^{-1}
4a	(103-107°C/0.05 mm)	(Found: C, 49.88; H, 6.48%; C$_{12}$H$_{18}$O$_8$ requires, C, 49.66; H, 6.21%); δ, 1.38 (12H, m), 4.38 (4H, q, J7Hz), 5.18 (2H, m); m/z 290.102 (M$^+$, 2.4%), C$_{12}$H$_{18}$O$_8$ requires 290.100; ν, 1770, 1750, 1310, 1185, 1015 cm^{-1}
4b	73-77°C	δ, 1.35 (6H, t, J7Hz), 1.69 (12H, s), 4.33 (4H, q, J7Hz); ν, 1760, 1315, 1185, 1135, 1020 cm^{-1}
4c	98-100°C	(Found: C, 68.93; H, 6.04; C$_{18}$H$_{18}$O$_5$ requires, C, 68.78; H, 5.77%); δ, 1.33 (3H, t, J7Hz), 2.31 (1H, broad, exchanges in D$_2$O), 4.27 (2H, q, J7Hz), 5.04 (1H, d, J6Hz), 5.93 (1H, d, J6Hz), 7.2 (10H, m); m/z, 314 (M$^+$, 16%), 180 (M-EtO$_2$C.CO$_2$-OH); ν, 3565, 1765, 1315, 1215, 710 cm^{-1}
4d (meso)	94-96°C	(Found: C, 63.93; H, 5.27%; C$_{22}$H$_{22}$O$_8$ requires, C, 63.77; H, 5.31%); δ, 1.34 (6H, t, J7Hz), 4.29 (4H, q, J7Hz), 6.23 (2H, s), 7.20 (10H, m); m/z, (no M$^+$),207 (M$^+$/2), 180 (M-2xO$_2$C.CO$_2$Et); ν, 1765, 1320, 1180, 1155, 700 cm^{-1}
4d (±)	93-95°C	(Found: C, 63.81; H, 5.43%); δ, 1.36 (6H, t, J7Hz), 4.31 (4H, q, J7Hz), 6.13 (2H, s), 7.2 (10H, m); m/z, 414 (M$^+$, 2%), 207 (M$^+$/2, 23%), 180 (M-2xO$_2$C.CO$_2$Et); ν, 1750, 1180, 1155, 700 cm^{-1}
4e (meso)	128-130°C	(Found: C, 70.77; H, 4.77; C$_{30}$H$_{22}$O$_8$ requires, C, 70.59; H, 4.31%); δ, 6.33 (2H, s), 7.0-7.5 (20H, m); m/z,(no M$^+$), 180 (stilbene, 53%), 94 (phenol, 100%); ν, 1740, 1200, 1160, 1140, 730 cm^{-1}
4f	115-118°C	(Found: C, 65.63; H, 4.37%; C$_{24}$H$_{18}$O$_8$ requires, C, 66.36; H, 4.15%); δ, 4.69 (1H, d, J5Hz), 4.70 (1H, d, J7Hz), 6.29 (1H, dd, J7Hz, J5Hz), 7.00-7.50 (15H, m); ν, 1785, 1750, 1335, 1300, 1180, 745 cm^{-1}
4g (meso)	90-01°	(Found: C, 54.89; H, 4.87%; C$_{18}$H$_{18}$O$_{10}$ requires, C, 54.83; H, 4.60%); δ 1.33 (6H, t, J7Hz), 4.28 (2H, q, J7Hz), 6.23-6.60 (4H, m), 6.55 (2H, s), 7.40-7.48 (2H, m); m/z, 394 (M$^+$, 3%), 277 (M-EtO$_2$C.CO, 2.9%), 160 (M-2xO$_2$C.CO$_2$Et, 25%); ν, 1745, 1015, 932, 882, 811 cm^{-1}
5d	65-66°C	δ, 5.65 (4H, s, PhCH$_2$), 7.40 (10H, s, ArH); m/z, 294 (M$^+$, 17%), 266 (M-CO, 2%), 238 (M-2xCO, 24%); ν, 1805, 1718, 1591, 750, 700 cm^{-1}
5e	103-105°C	(Found: C, 80.54; H, 5.05%; C$_{30}$H$_{22}$O$_4$ requires C, 80.69; H, 4.96%); δ, 5.73 (4H, s), 7.35-7.73 (18H, m); m/z, (no M$^+$), 168 (35%); ν, 1810, 1730, 1595, 760, 735, 700 cm^{-1}

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