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ELECTRO-ORGANIC REACTIONS. PART 28. PREPARATIVE APPLICATIONS OF THE OXALATE CATHODIC CLEAVAGE REACTION INCLUDING ONE-POT CONVERSIONS OF ALDEHYDES AND KETONES

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Abstract - Alcohols and vicinal diols, when co-electrolysed with oxalate esters, undergo transesterification catalysed by cathodically generated base. Under mild conditions at modest cathodic potentials the esters formed *in situ* give good yields of the corresponding alkanes and alkenes. Furthermore, because diols (pinacols) and alcohols may be efficiently prepared electrochemically from aldehydes and ketones, a one-pot conversion of the carbonyl compounds into alkanes and alkenes has been devised. The method involves prior electrolysis to alcohol or pinacol, addition of an oxalate ester, and further electrolysis for reductive de-oxygenation. Good results are obtained for aromatic ketones and aldehydes. Several oxalate esters have been used in such reactions; diethyloxalate is the most convenient. Esters of squaric acid and of oxamic acid undergo cathodic de-oxygenation but are not convenient in preparative use.

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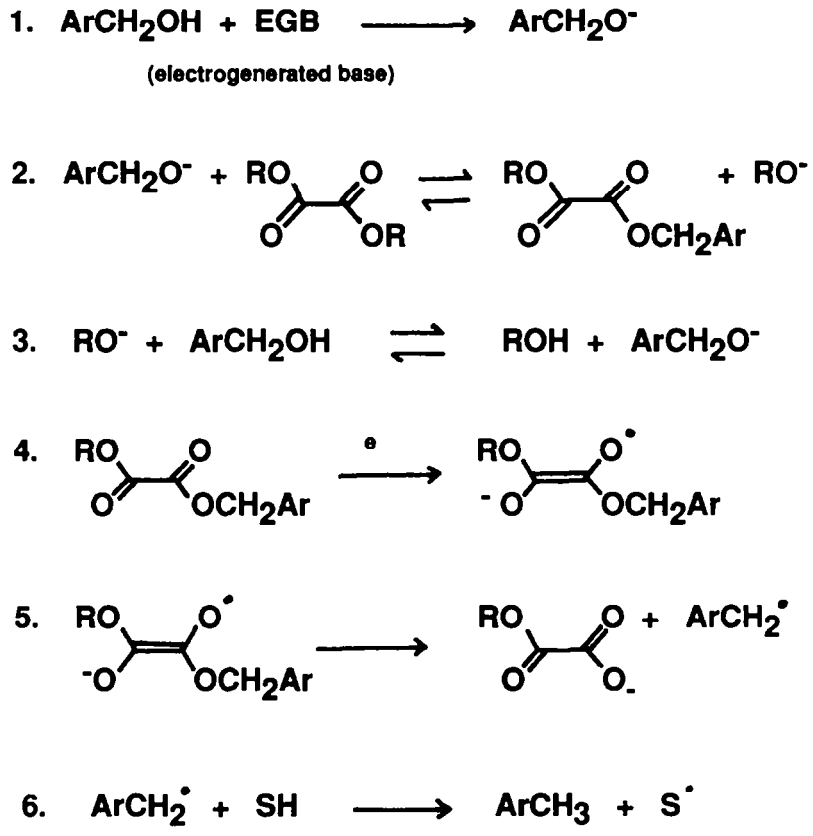
The cathodic reduction of oxalate esters has been shown[1] to result in carbon-oxygen bond cleavage. Oxalate reductions involve relatively low cathodic potentials in contrast to other cathodic cleavage reactions, in which the leaving groups are typically anions of strong acids[2] or which operate under strongly acidic conditions[3]. Furthermore, such esters are rapidly formed[4] in an electrochemical cell by *in situ* electrogenerated base-catalysed transesterification between an alcohol and a cheap oxalate ester, e.g. diethyl oxalate.



SCHEME 1.

The mechanism of the cathodic cleavage reaction was found[4] to be that given in Scheme 1. The anionic leaving group is the half-ester anion; the efficiency of the reaction, *vis à vis* competing hydrolysis, depends on the stability of the radical fragment. In practice this means that preparative applications are most likely to be found for cleavage from allylic and benzylic positions. We herein report on an extensive examination of these possibilities together with the successful combination of the cleavage reaction with prior reduction of ketones and aldehydes to give one-pot routes to, respectively, alkanes and alkenes.

Esters of 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid), and of oxamic acid, were found[4] to cleave by the same mechanism. They are less readily available than the corresponding oxalates but, nevertheless, examples of their reduction are included in this report.

RESULTS AND DISCUSSION

The deoxygenation of preformed esters: With the exception of the oxalate esters of hydrobenzoin it has been shown[4] that in most cases hydrolysis to the starting alcohol is faster than carbon-oxygen bond cleavage in the relevant radical-anions (see Scheme 1). On the possibly optimistic assumption[5] that the anions of strong acids are likely to be good leaving groups from radical-anions, the electrolysis of squarates and oxamates was examined. the results are given in Table 1, together with those from comparable experiments involving oxalate esters. The efficiency of carbon-oxygen cleavage is poor for all substrates except the oxalate of hydrobenzoin (5), [entry 5]; this reaction is different in that it involves cleavage driven by a rapid elimination step to give, exclusively, *trans*-stilbene. For cleavage from esters of monohydric alcohols the reaction is somewhat more efficient in dichloromethane solution, an observation which is consistent with the mechanism given in Scheme 1; H-atom abstraction is likely to be favoured under these conditions because the concentration of adventitious water will be lower in dichloromethane and it is also a good H-atom donor.

The precipitation of ester (3) during electrolysis of (4) in dichloromethane (entry 4) led to the realisation that rapid base-catalysed transesterification took place during the prolonged electrolyses. The mechanistic consequences of this have been discussed[4]. The observation also suggested a convenient method for forming the required esters by *in situ* transesterification which, because the alcohol formed by hydrolysis may be converted back into ester, can give good chemical yields even though current efficiencies remain low. The principle is illustrated in Scheme 2 wherein the use of an excess of a relatively accessible oxalate, e.g. diethyl oxalate, is assumed.

Deoxygenation following in situ formation of oxalates: The conditions for co-electrolysis of alcohols in the presence of diethyl oxalate were optimised for the production of diphenylmethane from benzhydrol and for toluene from benzyl alcohol (Table 2). The benzyl alcohol conversions indicated that reductive cleavage was likely to be more efficient in polar aprotic solvent, e.g. DMF rather than dichloromethane, and that a lead cathode works best. In contrast to the reduction of the preformed esters, (Table 1), the extra step of transesterification is required and it is possible that the more polar solvent is required for this to proceed rapidly. Experiments using benzhydrol as substrate show clearly that in this case the three electrode materials used, (Hg, Pb, C), work equally well and that the preferred solvents are DMF and MeCN. The addition of water, or the use of methanol as sovlent completely suppresses hydrocarbon formation, an observation which is consistent with the rapid hydrolysis/transesterification proposed in Scheme 1.

Table 1. Preparative Electrolysis of Pre-formed Oxalates, Squarates, and Oxamates

Entry	Ester	$-E_{red}$ [a]	Solvent/ Electrolyte [b]	% C-O Cleavage [c]
1.	$(PhCH_2O_2C-)_2$ (1)	1.30	DMF/TBAP	0
2.	$PhCH_2O_2C.CO_2Et$ (2)	1.30	DMF/TBAP	7
3.	$(4\text{-}Ph.C_6H_4CH_2O_2C-)_2$ (3)	1.20	DMF/TBAF	8
4.	$4\text{-}Ph.C_6H_4CH_2O_2C.CO_2Et$ (4)	1.60	CH_2Cl_2/TBAF	8
5.	PhCH(OX)CH(OX)Ph (5) (X = $OC.CO_2Et$)	1.20	DMF/TBAP	90 [d,e] 74 [d,f]
6.	$PhCH_2O_2CCONHPh$ (6)	1.33	MeCN/TBAI	19 [g]
7.	1,2-di-(4-phenylbenzylsquarate) (7)	1.50	CH_2Cl_2/TBAF	30
8.	1,2-dibenzylsquarate (8)	1.80	DMF/$LiClO_4$	6
9.	(8)	1.80	DMF/TBAI	11
10.	(8)	1.80	THF/TBAF	8
11.	(8)	1.80	CH_2Cl_2/TBAF	32

[a] Hg pool cathode, divided cell, V *vs* Ag/AgI, 1 $Fmol^{-1}$;

[b] TBAF = Bu_4NBF_4; TBAI = Bu_4NI; TBAP = Bu_4NClO_4;

[c] Yield of alkane, $ArCH_3$, by g.l.c. or ^1H n.m.r. analysis;

[d] *trans*-stilbene; [e] From (±)-isomer;

[f] From *meso*-isomer, isolated yield; [g] Aniline also detected

Several oxalate esters work well for this cleavage reaction (Table 2, entries 10-13). The use of diphenyloxalate offers the marginal advantage of requiring a slightly lower reduction potential. Di-t-butyl oxalate is less useful than the other esters studied; it is likely that in this case transesterification is slowed by steric factors.

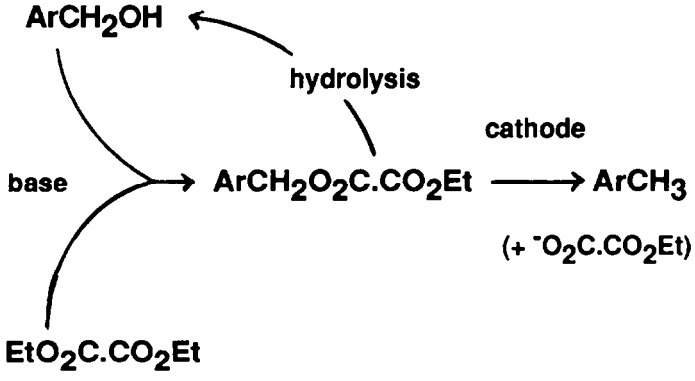
The optimised conditions determined by the experiments listed in Table 2 were used for the reductive deoxygenation of a selection of alcohols (Table 3). In each case diethyl oxalate was the accompanying ester and for convenience was used in all succeeding experiments. Satisfactory isolated yields of the corresponding alkanes were obtained when the hydroxyl function was benzylic. In the case of triphenylmethanol cleavage was less efficient and, again, it is likely that the necessary prior esterification is sterically hindered. The reaction works poorly for cinnamyl alcohol and benzoin and not at all for 3-phenylpropanol. The latter result is explained by the absence of any stabilisation of the intermediate radical. The benzoin result is probably due to competing electroreduction; the alcohol is itself reduced at near to -1.55V.

The formation of both stilbene (exclusively *trans*) and 1,2-diphenylethane by co-electroysis of diethyl oxalate with either *meso* or (±) hydrobenzoin (entry 6) indicates stepwise reactions which can involve initial formation of diesters or monoesters (Scheme 3). Concerted cleavage from the diester would be expected to give *trans*-stilbene from the *meso*-isomer and *cis*-stilbene from the (±) isomer. It was shown by separate electrolysis that *trans*-stilbene is not reduced under the conditions of electrolysis. The best conversion of this type involved co-electrolysis of the *meso*-ester (5) with a two-fold excess of diethyl oxalate which, in MeCN-TBAB solution at a lead cathode gave 81% conversion (65% *trans*-stilbene and 16% 1,2-diphenylethane [bibenzyl]).

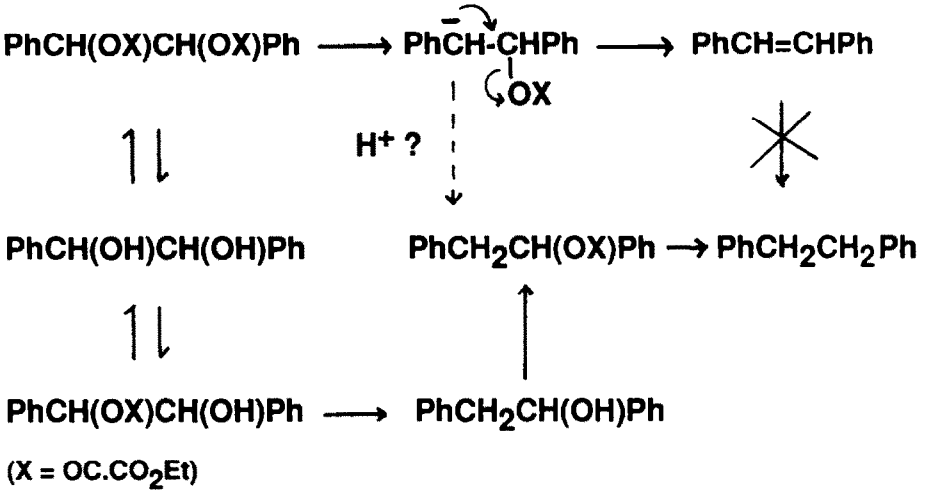
Table 2. Optimisation Experiments: Co-electrolysis of Alcohols and Oxalates

Entry	Alcohol	Ester	$-E_{red}$ [b]	Solvent/ electrolyte/ electrode	% C-O Cleavage
1.	benzyl alcohol	diethyl oxalate	1.60	CH_2Cl_2, TBAF, Hg	32[c]
2.	benzyl alcohol	diethyl oxalate	1.60	DMF, TBAF, Hg	30[c]
3.	benzyl alcohol	diethyl oxalate	1.60	DMF, TBAF, Pb	73[c]
4.	benzyl alcohol	diethyl oxalate	1.55	DMF, TBAF, Pb	70[d]
5.	benzyl alcohol	diethyl oxalate	1.55	DMF, TBAB, Pb	72[d]
6.	diphenylmethanol	diethyl oxalate	1.55	MeCN, TBAB, Pb	68[d]
7.	diphenylmethanol	diethyl oxalate	1.55	MeCN, TBAB, Hg	69[d]
8.	diphenylmethanol	diethyl oxalate	1.55	MeCN, TBAB, C	69[d]
9.	diphenylmethanol	diethyl oxalate	1.55	MeOH, TBAB, Pb	0
10.	diphenylmethanol	dimethyl oxalate	1.55	MeCN, TBAB, Pb	68[d]
11.	diphenylmethanol	diphenyl oxalate	1.40	MeCN, TBAB, Pb	70[d]
12.	diphenylmethanol	di-*iso*propyl oxalate	1.65	MeCN, TBAB, Pb	72[d]
13.	diphenylmethanol	di-*t*-butyl oxalate	1.75	MeCN, TBAB, Pb	50[d]
14.	diphenylmethanol	ethyl oxamate	1.80	MeCN, TBAB, Pb	40[d]

[a] Divided cell, 2 molar equivalents of ester, 1 $Fmol^{-1}$ w.r.t. ester; TBAB = Bu_4NBr; [b] V *vs* $Ag/AgI_{(s)}$; [c] g.l.c. analysis; [d] isolated product



SCHEME 2.



SCHEME 3.

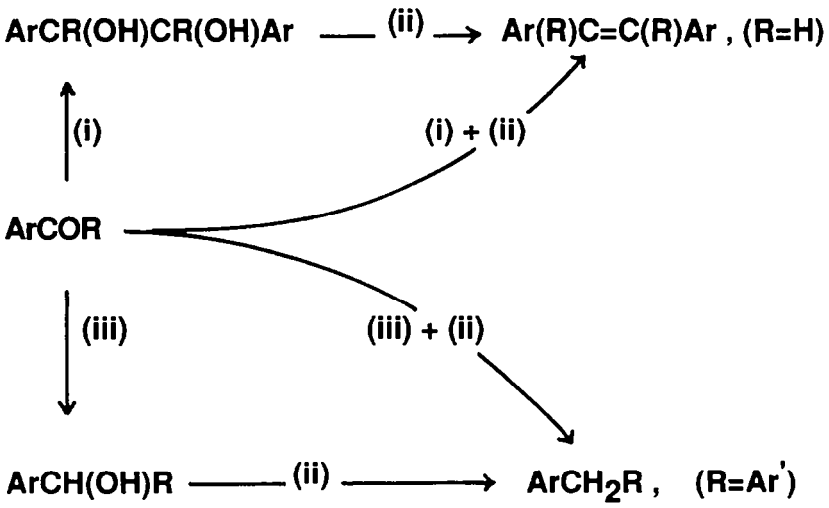
Table 3. Reductive Deoxygenation *via* transesterification[a]

Entry	Alcohol	% C-O Cleavage
1.	4-Ph.$C_6H_4CH_2OH$	63[b]
2.	4-Me.$C_6H_4CH_2OH$	69[c]
3.	PhCH:$CHCH_2OH$	30[b]
4.	$PhCH(OH)CH_2Ph$	68[c]
5.	PhCH(OH)COPh	30[b]
6.	PhCH(OH)CH(OH)Ph[d]	58[c,e]
7.	$PhCH_2CH_2CH_2OH$	0[c]
8.	Ph_2CHOH	70[b,c]
9.	Ph_3COH	50[b]
10.	3-pyridylmethanol	72[c]
11.	2-naphthylmethanol	70[b]

[a] Divided cell, -1.55 *vs* $Ag/AgI_{(s)}$, Pb cathode, diethyl oxalate (2 molar equivalents), 1 $Fmol^{-1}$ w.r.t. ester;

[b] DMF-TBAF (0.1M); [c] MeCN-TBAB (0.1M); [d] *meso* or (±);

[e] *trans*-stilbene (47%) and 1,2-diphenylethane (11%) - very similar results obtained from co-electrolysis using oxalate esters listed in Table 2, entries 10-13.



(i) **Divided cell, Pb cathode, MeCN/TBAB(0.1M)/$(CO_2H)_2$[1 equiv.], -1.55V (Ag/AgI(s)), 1 $Fmol^{-1}$.**

(ii) **Addition of diethyl oxalate [2 equiv.], further 1 $Fmol^{-1}$.**

(iii) **Divided cell, Hg cathode, MeCN/TBAB(0.1M)/HOAc[2 equiv.], -1.30V, 2 $Fmol^{-1}$.**

SCHEME 4.

The one-pot conversion of carbonyl compounds into alkanes and alkenes: Aromatic aldehydes are conveniently pinacolised electrochemically[6]. In contrast aromatic ketones undergo electro-reduction to the corresponding alcohols except in strongly acidic media, or in the presence of chromium trichloride[7]. The carbonyl reduction reactions have here been coupled with the oxalate de-oxygenation reaction and the possibilities for one-pot reaction are given in Scheme 4 with the result for several examples being listed in Table 4. It is possible to stop reaction at the first stage and isolate pinacols or alcohols in good yield; however, addition of a two-fold excess of diethyl oxalate and further electrolysis allows the second reduction step, de-oxygenation, to proceed in the same cell. The experimental procedure is simple and convenient. In Table 4 the results given refer to both possibilities, i.e. the pinacol and alcohol columns are for isolation after the first step and the alkene and alkane columns refer to products isolated after sequential one-pot electrolysis.

Furfural is known[8] to be similar to benzaldehyde in its electrochemical reductive behaviour. It is also an important intermediate which may be produced cheaply and on a large scale from biomass. Consequently cathodic conversions of furfural and its derivatives, including application of the oxalate reduction method, have been studied separately and in detail. Several useful transformations resulted which are reported elsewhere[9].

Table 4. One-pot Reductive De-oxygenation of Aromatic Aldehydes and Ketones[a]

Entry	Ketone	Aldehyde	% Pinacol	% Alcohol	% Alkene	% Alkane
1.		PhCHO	73		43	
2.	Ph_2CO			83		70
3.		4-Me.C_6H_4CHO	72		57	
4.	4-Me.C_6H_4COPh			80		73
5.		4-MeO.C_6H_4CHO	73		57	
6.	Fluorenone[b]			82		65

[a] Reaction conditions given in Scheme 4; isolated yields.

[b] First step reduction potential -0.9V (Ag/AgI)

EXPERIMENTAL

Starting materials: The preparation of the pre-formed oxalates (1) to (5) and oxamate (6) involved reaction between the alcohol or amine and, as appropriate, oxalyl chloride, ethyl oxalyl chloride, or phenyl oxalyl chloride. The squarate esters (7) and (8) were prepared from disilver squarate and the corresponding benzyl chloride. These preparations and physical data pertaining to new compounds have been reported in detail[4].

Electrochemical experiments: Equipment, and the methods used for purification of solvents and electrolytes, were as described in earlier papers in the series. Reaction conditions are detailed in footnotes to the Tables 1-4.

The following preparative-scale electrolyses are typical of the procedures followed. None of the products were new compounds and they were unambiguously identified by comparison of spectroscopic data and physical constants with those reported or with those of authentic samples.

meso-1,2-Bis(ethoxalyloxy)-1,2-diphenylethane (5): (1.43g, 0.0035 mol) was reduced at a lead plate cathode (area 8 cm^2), at -1.55V (*vs.* $Ag/AgI_{(s)}$), in a divided cell of catholyte volume 50cm^3. The electrolyte was MeCN-Bu_4NBr (0.1M). After 2 $Fmol^{-1}$ had been consumed the catholyte solvent was removed by evaporation under reduced pressure and water (20cm^3) added. The product was extracted into ether and treated with aqueous NaOH (2M) for 3 hours. Isolation in the usual way gave ***trans*-stilbene** (0.46g, 74%).

meso-1,2-Diphenylethane-1,2-diol (hydrobenzoin) (1.0g, 0.0047 mol) and diethyl oxalate (2.05g, 0.0014 mol) were electrolysed at -1.55V for 1 $Fmol^{-1}$, w.r.t. the oxalate, using the cell and reaction conditions described above. Similar aqueous work-up yielded a solid (0.5g) which was shown by ^1H n.m.r. spectroscopic examination to be ***trans*-stilbene** (47%) and **bibenzyl** (11%).

4-Methoxybenzaldehyde (1.04g, 0.0077 mol) and oxalic acid (0.41g, 0.0046 mol) were electrolysed at -1.55V at a lead cathode as described above. After 0.9 $Fmol^{-1}$ had passed, diethyl oxalate (2.80g, 0.0192 mol) was added to the catholyte and electrolysis continued for a further 1.1 $Fmol^{-1}$. Aqueous work-up gave ***trans*-4,4'-dimethoxystilbene** (0.5g, 57%).

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REFERENCES

1. D.W. Sopher and J.H.P. Utley, *J. Chem. Soc., Chem. Commun.*, 1981, 134.

2. J.P. Coleman, Naser-ud-din, H.G. Gilde, J.H.P. Utley, B.C.L. Weedon and L. Eberson, *J. Chem. Soc., Perkin Trans. 2*, 1973; 1903; T. Shono, Y. Matsumura, K. Tsubata, and Y. Sugihara, *Tetrahedron Lett.*, 1979, 2157; *idem, J. Org. Chem.*, 1979, **44**, 4508.

3. T. Lund and H. Lund, *Acta Chem. Scand.*, 1984, **B38**, 387.

4. N. Islam, D.W. Sopher and J.H.P. Utley, *Tetrahedron*, 1987, in press.

5. C.J.M. Stirling, *Acc. Chem. Res.*, 1979, **12**, 198; U. Akbulut, L. Toppare and J.H.P. Utley, *J. Chem. Soc., Perkin Trans. 2*, 1982, 391; V.L. Pardini, L. Roullier, J.H.P. Utley and A. Webber, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1520; N. Berenjian and J.H.P. Utley, *J. Chem. Soc., Chem. Commun.*, 1979, 550.

6. L.G. Feoktistov and H. Lund, in *Organic Electrochemistry, ed.* M.M. Baizer and H. Lund, Chapter 9, Dekker, N.Y., 1983.

7. D.W. Sopher and J.H.P. Utley, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1361.

8. W.C. Albert and A. Lowy, *Trans. Electrochem. Soc.*, 1939, **75** 367.

9. K.G. Ellis, N. Islam, D.W. Sopher, J.H.P. Utley, H.L. Chum and M. Ratcliff, *J. Electrochem. Soc.*, 1987, in press.