The Electrochemical Reductive Cleavage of Carbon–Oxygen and Carbon–Fluorine Bonds in Benzyl Systems

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Summary The cathodic reduction of cyano- or methoxycarbonyl-substituted benzyl methyl ether, benzyl acetate, and benzylidyne trifluoride probably involves electron transfer to the substituent with subsequent cleavage of C–O or C–F bonds.

BENZYL methyl ether and its derivatives with an electron-releasing substituent undergo side-chain oxidation on electrolysis in methanol. Under similar conditions the *o*- or *p*-methoxycarbonyl and *p*-cyano-derivatives are reduced to the corresponding toluenes.[1] We now report studies which clarify this marked difference in behaviour, and extend the reduction to the cleavage of C–F bonds.

Methanolic solutions (0·2 M) of the compounds in Table 1 were electrolysed at controlled cathode potential in the presence of tetra-n-butylammonium acetate (0·5 M). An undivided cell was used with a platinum anode and a lead or mercury cathode. The direct involvement of the electro-active substituents is indicated by the high efficiency for fluorine loss from the *p*-methoxycarbonyl-substituted compound (IV) compared with the corresponding *m*-isomer (VI). Cyano and carbonyl functions may be reduced electrochemically, but we find only a small proportion of such a product (XII). The major products from the methoxycarbonyl-substituted compounds are probably formed according to Scheme 1 (in which the first two steps might be concerted), and those from the cyano-substituted systems by an analogous route. Where R = F the sequence can be repeated twice more. The electrochemical cleavage of the C–F bond in phenacyl fluoride has been shown by polarography to involve the transfer of two electrons.[2]

TABLE 1

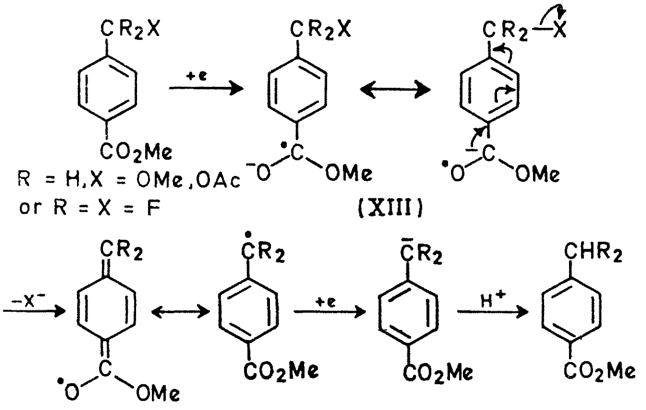
Starting material	Cathode (potential v *vs* S.C.E.)	Product[a]	Yield (%)[b]	Current efficiency (%)
p-MeO$_2$C·C$_6$H$_4$·CH$_2$OMe (I)	Pb (−1·9)	*p*-MeO$_2$C·C$_6$H$_4$Me (VII)	79	68
	Hg (−1·9)	(VII)	78	71
p-MeO$_2$C·C$_6$H$_4$·CH$_2$OAc (II)	Pb (−1·8)	(VII)	95	76
BzCH$_2$OAc (III)	Pb (−1·8)	BzMe (VIII)	20	11
		PhCH(OH)Me (IX)	54	56
p-MeO$_2$C·C$_6$H$_4$·CF$_3$ (IV)	Pb (−2·0)	(VII)	60[c]	52
p-NC·C$_6$H$_4$·CF$_3$ (V)	Pb (−1·8)	*p*-NC·C$_6$H$_4$Me (X)	58[c]	54
m-MeO$_2$C·C$_6$H$_4$·CF$_3$ (VI)	Pb (−2·0)	*m*-MeO$_2$C·C$_6$H$_4$Me (XI)	11[c,d]	13
		m-HOCH$_2$·C$_6$H$_4$·CF$_3$ (XII)	*ca* 5	*ca* 5

[a] Products (VII)—(X) isolated and identified by comparison of g.l.c. retention times and i.r. and n.m.r. spectra with those of authentic specimens, (XI) and (XII) by retention times on two columns.

[b] Absolute yield calculated from g.l.c. of products after addition of internal standard, based on starting material consumed, judged accurate to ±5% of values quoted.

[c] No products with partial loss of fluorine were detected (*cf.* ref. 3).

[d] Other, possibly dimeric products formed, with apparently no loss of fluorine.



SCHEME 1

Further evidence for Scheme 1 comes from experiments in the presence of acetic acid. A solution of compound (I) in dry methanol was electrolysed at constant current density (0·15 A cm^{-2}) in the presence of anhydrous sodium acetate (0·5 M) and acetic acid (0·5 M) using a lead cathode (potential −1·5 to −1·8 v, *vs* S.C.E.). The results of product analysis are given in Table 2. We suggest that in

TABLE 2

Electrolysis of (I) *in the presence of acetic acid*

Product[a]		Relative yield (%)
Recovered starting material (I)	..	11
p-MeC$_6$H$_4$·CHO (XIV)	..	13
p-MeC$_6$H$_4$·CO$_2$Me (VII)	..	21
p-MeC$_6$H$_4$·CH$_2$OH (XV)		17
p-MeOCH$_2$·C$_6$H$_4$·CHO (XVI)		11
p-MeOCH$_2$·C$_6$H$_4$·CH$_2$OH[b] (XVII)		27

[a] Identified by comparison of g.l.c. retention times with those of authentic samples.

[b] Isolated and identified by comparison of spectroscopic properties with those of an authentic sample.

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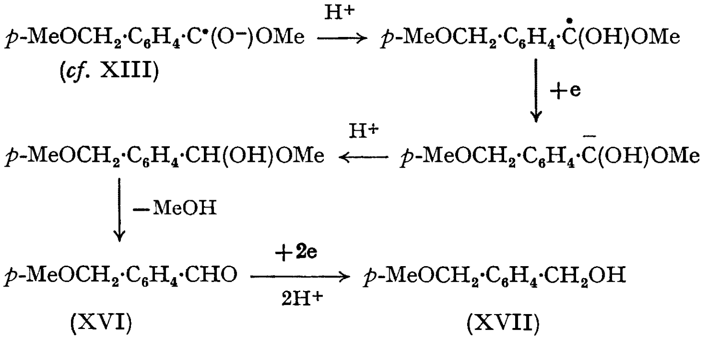


$$\begin{tikzcd}
p\text{-MeOCH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}^{\bullet}(\text{O}^-)\text{OMe} \arrow[r, "\text{H}^+"] & p\text{-MeOCH}_2\cdot\text{C}_6\text{H}_4\cdot\overset{\bullet}{\text{C}}(\text{OH})\text{OMe} \arrow[d, "+\text{e}"] \\
p\text{-MeOCH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\text{OMe} \arrow[d, "-\text{MeOH}"] & p\text{-MeOCH}_2\cdot\text{C}_6\text{H}_4\cdot\overset{-}{\text{C}}(\text{OH})\text{OMe} \arrow[l, "\text{H}^+"'] \\
p\text{-MeOCH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO} \arrow[r, "+2\text{e}", "2\text{H}^+"'] & p\text{-MeOCH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{OH}
\end{tikzcd}$$

(cf. XIII)

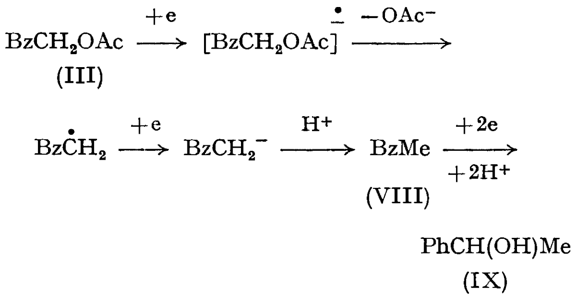
(XVI) (XVII)

SCHEME 2

the presence of acetic acid either the protonated starting material is discharged, or that the intermediate (XIII) is trapped efficiently. We consider the latter possibility more likely because of the similarity of the cathode potentials necessary for reaction with and without added acetic acid. The products (XVI) and (XVII) are therefore rationalised by Scheme 2, and an analogous scheme may be drawn to explain the formation of (XIV) and (XV) from methyl *p*-toluate (VII) which would be formed by the competing Scheme 1.

Another example of the participation of a suitably placed electroactive substituent is the ready elimination of acetate upon electroreduction of phenacyl acetate (III), presumably according to Scheme 3 in neutral or basic media.

Other reactions[2,3] where cleavage of C–O or C–F has been induced electrochemically may be rationalised similarly.



$$\begin{tikzcd}
\text{BzCH}_2\text{OAc} \arrow[r, "+\text{e}"] & {[\text{BzCH}_2\text{OAc}]^{\overset{\bullet}{-}}} \arrow[r, "-\text{OAc}^-"] & {} \\
\text{Bz}\overset{\bullet}{\text{C}}\text{H}_2 \arrow[r, "+\text{e}"] & \text{BzCH}_2^- \arrow[r, "\text{H}^+"] & \text{BzMe} \arrow[r, "+2\text{e}", "+2\text{H}^+"'] & {} \\
 & & & \text{PhCH(OH)Me}
\end{tikzcd}$$

(III)

(VIII)

(IX)

SCHEME 3

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[2] P. J. Elving and J. T. Leone, *J. Amer. Chem. Soc.*, 1957, **79**, 1546.

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