Electrochemical Synthesis of 2-Methoxy-1,4-dioxans by Anodic Oxidation of $\beta\textsc{-}Oxocarboxylate$ Ethylene Acetals

By Daniel Lelandais, Cathy Bacquet, and Jacques Einhorn (Laboratoire de Chimie Organique Structurale, Université Pierre et Marie Curie, Batiment F, 4, place Jussieu, 75230 Paris Cedex 05, France)

Summary Anodic oxidation of the β -oxocarboxylate ethylene acetals (1a—e) in anhydrous methanol gives the 2-methoxy-1,4-dioxans (2a—e) in 40—60% yield.

OXIDATIVE substitution is a type of reaction which is of current interest, and the Kolbe reaction, producing carbonium ions, should provide a good means for carrying out such reactions. In view of our interest in this area, 2

we have studied the anodic oxidation of the β -oxocarboxylate ethylene acetals (1a-e), giving the 2-methoxy-1,4dioxans (2a-e).3

TABLE. Electrolysis of (1) to give (2).

	Carboxylate (1)			% Yield
	$\mathbf{R^{1}}$	$\tilde{\mathbf{R}^2}$	R^3	of (2)
a	Me	H	H	4 Ò ′
b	Me	Me	\mathbf{H}	40
c	Me	Me	Me	45
d	Me	Et	\mathbf{H}	60
e	$-[CH_{2}]_{3}-$		H	40

Electrolyses were carried out for 1m solutions of the potassium carboxylates in anhydrous methanol in an undivided cell with a graphite anode at a potential > 2 V (current density $ca. 0.2 \text{ A cm}^{-2}$). The products obtained (Table) were characterized by n.m.r. and mass spectroscopy. Compounds (2b) and (2d) were obtained as 1:1 mixtures

(g.l.c.) of diastereoisomers, which have been separated. Attempts are being made to separate the isomers of (2e). We suggest the mechanism in the Scheme for this reaction.

$$\begin{array}{c}
\begin{pmatrix}
O \\
O
\end{pmatrix} CR^{1} - CR^{2}R^{3} - CO_{2}^{-} & K^{+} \xrightarrow{-2e} & O \\
& R^{1}
\end{array}$$

$$\begin{array}{c}
O \\
& CR^{1} - \overrightarrow{C}R^{2}R^{3} \\
& O \\
& R^{2}
\end{array}$$

$$\begin{array}{c}
O \\
& R^{1} \\
& O \\
& R^{3}R^{2}
\end{array}$$

$$\begin{array}{c}
O \\
& R^{1} \\
& O \\
& R^{3}R^{2}
\end{array}$$

$$\begin{array}{c}
O \\
& R^{1}
\end{array}$$

$$\begin{array}{c}
O \\
& R^{2}
\end{array}$$

$$\begin{array}{c}
O \\
& R^{2}
\end{array}$$

$$\begin{array}{c}
O \\
& R^{2}
\end{array}$$

$$\begin{array}{c}
O \\
& R^{3}
\end{array}$$

SCHEME

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